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ARTICLE TYPE

Synthesis of push–pull chromophores by the sequential [2 + 2] cycloaddition of 1-azulenylbutadiynes with tetracyanoethylene and tetrathiafulvalene

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The azulene-substituted butadiynes have been prepared by Cu-mediated cross- and homo-coupling reaction. The azulene-substituted butadiynes reacted with tetracyanoethylene in a formal [2 + 2] cycloaddition reaction to afford the corresponding 1,1,4,4-tetracyanobutadiene chromophores, respectively, in excellent yields. Further [2 + 2] cycloaddition with TTF and TCNE gave novel donor–acceptor chromophores and novel azulene-substituted 6,6-dicyanofulvene derivative.

Introduction

Tetrathiafulvalene (TTF) is well known as a powerful electron donor to form CT complexes with a variety of electron-deficient organic compounds because of the formation of stable aromatic 1,3-dithiole rings by one- or two-electron oxidation. Thus, TTF and its derivatives have attracted much attention as conductive components of molecular conductors.¹

At the first time, Hopf et al. have reported the [2 + 2] cycloaddition reaction of TTF, a strong electron donor, with electron-deficient acetylenes with dicyanoethylene substituent to afford 1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives with dicyanoethylene substituent.² As an extension of this study, Diederich et al. have reported the sequential [2 + 2] cycloaddition reaction of tetracyanoethylene (TCNE) and TTF with dialkylamino- (DAA-) substituted electron-rich butadiynes yielding multivalent charge-transfer (CT) chromophores, tetracyanobutadiene (TCBD)/1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives, that are capable of taking up an exceptional number of electrons under electrochemical conditions.³

Azulene (C₁₀H₈) has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.⁴ Recently, we have also reported the reaction of poly(1-azulenylethynyl)benzene and thiophene derivatives with TCNE and TCNQ to give the corresponding intramolecular CT chromophores, which exhibit a multistep reduction wave on cyclic voltammetry (CV), in excellent yields.⁵

Previously, Hafner et al. reported the preparation of 1-azulenylbutadiynes utilizing a Cu-mediated oxidative coupling under Eglinton conditions.⁶ Although 1-azulenylbutadiynes are one of promising building blocks for the construction of novel CT chromophores, reactivity of their derivatives is not energetically investigated so far. As similar to the DAA-substituent, 1-position

of azulene ring possesses strong electron-donating properties with high reactivity toward electrophilic substitution reactions. Thus, butadiyne derivatives substituted by 1-azulenyl moiety should be expected to afford a new series of donor–acceptor chromophores by the sequential [2 + 2] cycloaddition reactions with TCNE and TTF. Furthermore, azulene-substituted donor–acceptor chromophores may exhibit multistage amphoteric redox behaviour with redox reaction of the azulene core.

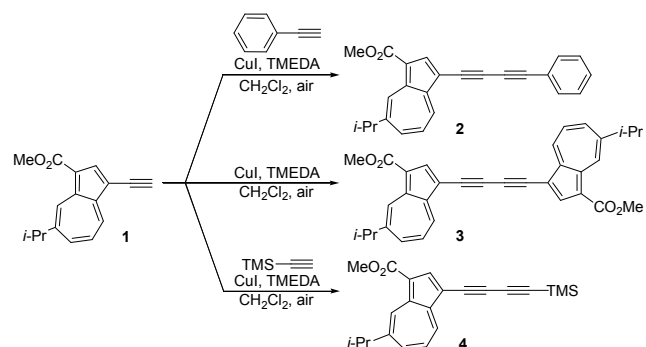
Herein, we report the synthesis of novel azulene-substituted donor–acceptor chromophores by the sequential [2 + 2] cycloaddition of 1-azulenylbutadiynes with TCNE and TTF, as well as spectroscopic and electrochemical properties of the novel donor–acceptor chromophores clarified by UV/Vis spectrometry and electrochemical analysis.

Results and discussion

Synthesis

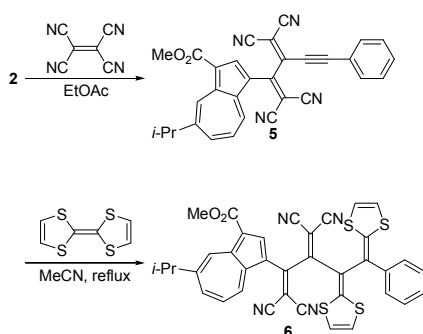
Preparation of azulene-substituted butadiene derivatives, i.e., methyl 7-isopropyl-3-(4-phenylbuta-1,3-dienyl)azulene-1-carboxylate (**2**), 1,4-bis(7-isopropyl-1-methoxycarbonylazulen-3-yl)buta-1,3-diyne (**3**), and methyl 7-isopropyl-3-(4-trimethylsilylbuta-1,3-dienyl)azulene-1-carboxylate (**4**) was investigated by Cu-mediated Hay⁷ cross- and Glaser⁸ homo-coupling conditions, respectively (Scheme 1). The cross-coupling reaction of methyl 7-isopropyl-3-ethynylazulene-1-carboxylate (**1**)⁵ with 5 equiv. of ethynylbenzene, using CuI/tetramethylethylenediamine (TMEDA) as the catalysts, and subsequent chromatographic purification on silica gel afforded the desired **2** in 74% yield, along with the homo-coupling product **3** in 20% yield. Compound **3** was also obtained in 91% yield as a sole product, by the Glaser homo-coupling reaction of **1** under the similar reaction conditions. Similar with the synthesis of **2**, butadiyne **4** was obtained by the reaction of **1** with 5 equiv. trimethylsilylacetylene in 76% yield, along with **3** in 17% yield. These butadiyne derivatives **2**, **3** and **4** possess fair solubility in

chloroform, dichloromethane, and so on. Moreover, they are stable and showing no decomposition, even after several weeks at room temperature. Thus, these butadiyne derivatives could be utilized in further transformations for the synthesis of novel donor–acceptor chromophores owing to their considerable stability and solubility.



Scheme 1 Synthesis of 1-azulenylbutadiynes **2**, **3** and **4**.

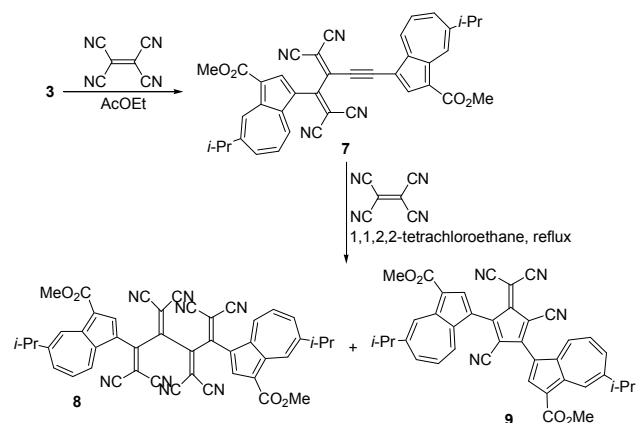
The sequential [2 + 2] cycloaddition reaction of **2** and **3** with TCNE and TTF was examined for the construction of novel donor–acceptor chromophores. Thus, the reaction of **2** with TCNE was examined in ethyl acetate at room temperature to yield **5** in 95% yield.^{3,5,9} Subsequent [2 + 2] cycloaddition reaction of **5** with excess TCNE in the remaining ethynyl moiety, contiguous to the phenyl group, did not proceed even under the refluxing conditions in DMF. These results indicate the low reactivity of the C≡C triple bond attached to the highly electron-withdrawing TCBD moiety. The synthesis of the TCNE/TTF double adduct **6** was achieved in 92% yield by the [2 + 2] cycloaddition reaction of **5** with TTF (Scheme 2). The one-pot cascade reaction of **2** with TCNE and TTF also gave **6** in 70% yield, which corresponds to 84% yield in each step. However, the cascade reaction requires a tedious separation process.



Scheme 2

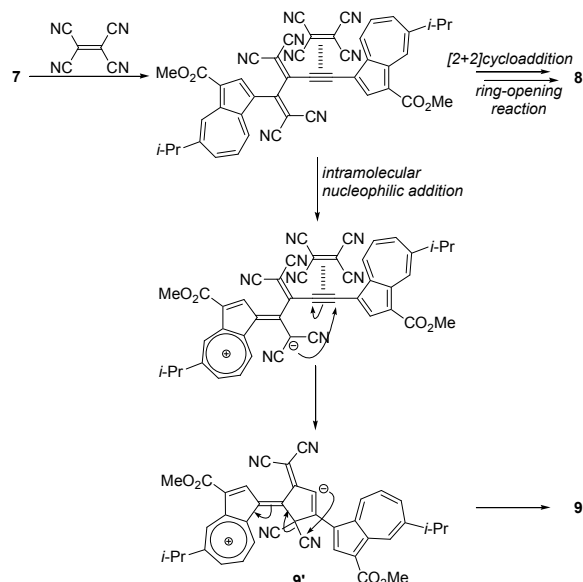
Likewise, the reaction of butadiyne **3** with TCNE at room temperature afforded TCBD **7** in 97% yield. Although the resulting **7** was treated with TTF, the corresponding TCNE/TTF double-adduct could not be obtained, but resulting into the recovery of the TCBD **7**. Meanwhile, subsequent [2 + 2] cycloaddition of **7** with TCNE was observed under the refluxing conditions in 1,1,2,2-tetrachloroethane to afford the double TCNE-adduct **8** in 71% yield, along with novel 6,6-

dicyanofulvene derivative **9** in 22% yield (Scheme 3).



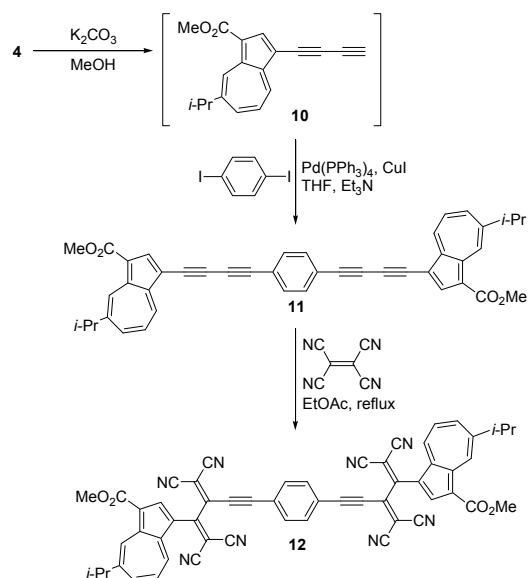
Scheme 3

When the compounds **7** and **8** were refluxed in 1,1,2,2-tetrachloroethane without TCNE, 6,6-dicyanofulvene **9** could not be obtained, but resulting into the recovery of the starting compounds **7** and **8**. Thus, TCNE has important role for the formation of 6,6-dicyanofulvene derivative **9**. The presumed reaction mechanism for the formation of **8** and **9** is illustrated in Scheme 4. This reaction should involve two reaction pathways to afford **8** and **9**. Initially, TCNE exhibits coordination to **7** with electron-rich acetylene moiety attached to 1-azulenyl group. In one pathway, the TCNE molecule undergoes [2 + 2] cycloaddition with the acetylene moiety of **7** to afford the cyclobutene intermediate. Subsequent ring-opening reaction of the cyclobutene derivative gives the thermodynamically stable TCBD derivative **8**.¹⁰ As another mechanism, the dicyanomethylidene group attached to the azulene ring in **7**, which has certain electronegativity by the conjugation with 1-azulenyl group, attacks to intramolecular acetylene moiety with a decreased LUMO-level by the TCNE coordination, to form a five-membered ring of **9**. In the generated zwitter ionic species **9**⁺, the migration of a cyano group results into the formation of 6,6-dicyanofulvene derivative **9**.¹¹ Recently, Diederich et al. have reported the first synthesis of donor-substituted 6,6-dicyanofulvene derivative with interesting optoelectronic properties.¹² In the view point of azulene chemistry, compound **9** is the first example of 6,6'-dicyanofulvene derivative substituted by azulene ring.



Scheme 4 Presumed reaction mechanism for the formation of **8** and **9**.

Compounds **11** was prepared by the Pd-catalyzed alkylation of 1,4-diiodobenzene with butadiyne **10**, which was prepared by the desilylation of **4**, under Sonogashira–Hagihara conditions (Scheme 5). A solution of **4** in methanol was treated with a potassium carbonate solution to generate the corresponding butadiyne **10**. The green solid **10** decomposed at room temperature, but has certain stability in solution to be employed for further transformation. The cross-coupling reaction of **10** with 1,4-diiodobenzene using Pd(PPh₃)₄ as a catalyst, and subsequent chromatographic purification of the reaction mixture on silica gel, afforded the desired **11** in 87% yield. As similar to the results on the butadiynes **2** and **3**, the reaction of **11** with TCNE afforded bis-adduct **12** in 95% yield. To the synthesis of the TCNE/TTF double adduct, the [2 + 2] cycloaddition reaction of **12** with TTF was also examined under the similar conditions for the preparation of **6**. However, in contrast to the results on the reaction of **6**, the reaction of **12** with TTF formed an insoluble complex mixture. It should be attributed to instability of the compound under the reaction conditions.



Scheme 5

25 Spectroscopic Properties

The structure of these novel compounds **2–12** was confirmed by spectral data including ¹H, ¹³C NMR, HMQC, HMBC and NOE experiments, except for **10**. The absorption maxima (λ_{max}) and their coefficients (log ε) of the new compounds **5–9** and **12** are summarized in Table 1.

Table 1 Absorption maxima [nm] and their coefficients (log ε) of DCNQ chromophores **10–18** in dichloromethane and in 10% CH₂Cl₂/hexane.

Sample	λ _{max} (log ε) in CH ₂ Cl ₂	λ _{max} (log ε) in hexane
5	388 (4.47), 530 (3.93)	513 (3.87) ^a
6	471 (4.52)	463 (4.48) ^a
7	394 (4.33), 545 (4.52)	392 (4.29), 515 (4.49) ^a
8	450 (4.40), 510 sh (4.19)	419 (4.25), 438 (4.24), 488 sh (4.17) ^a
9	542 sh (4.03), 583 (4.11), 808 (3.64)	530 sh (4.04), 570 (4.11), 755 (3.50) ^a
12	443 (4.46), 544 sh (4.11)	438 (4.46), 544 sh (4.04) ^b

^a Dichloromethane (10%) was included to keep the solubility of these compounds. ^b Dichloromethane (20%) was included to keep the solubility of these compounds.

The UV/Vis spectra of butadiynes **2**, **3**, **4** and **11** showed weak characteristic absorption bands arising from the azulene moiety in the visible region. As expected from their structures, TCBD derivatives, TCNE/TTF double-adduct **6** and 6,6-dicyanofulvene **9** showed relatively strong CT absorption bands in the visible region (Figures 1–3). The spectrum of **5** in dichloromethane displayed a characteristic CT absorption band at λ_{max} = 530 nm (log ε = 3.93). The UV/Vis spectrum of **6** exhibited strong and broad absorption band at λ_{max} = 471 nm in dichloromethane, which might be reflected to the overlapping of the CT absorption bands between two-donor moieties [i.e., azulene and 1,2-bis(1,3-dithiol-2-ylidene)ethane] and TCBD-acceptor unit (Figure 1).

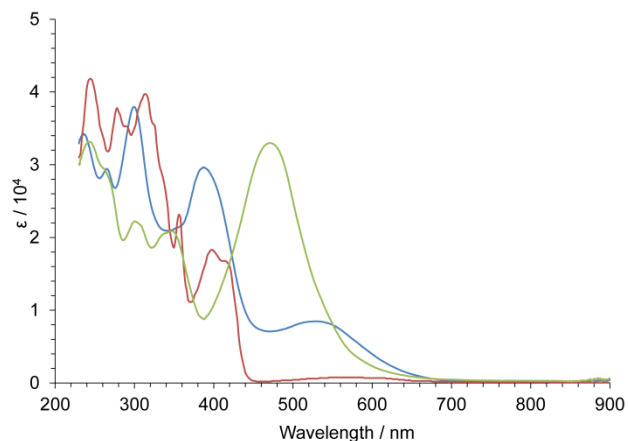


Fig. 1 UV/Vis spectra of **2** (blue line), **5** (red line) and **6** (green line) in dichloromethane.

Compound **7** exhibited two CT absorption bands at $\lambda_{\text{max}} = 394$ nm (weak) and $\lambda_{\text{max}} = 545$ nm (strong) in dichloromethane (Figure 2). The longest absorption of **7** displayed a bathochromic shift by 15 nm compared with that of **5** ($\lambda_{\text{max}} = 530$ nm). These results indicate that the π -conjugation is efficiently expanded by the 1-azulenyl group rather than phenyl group substituted. Broad CT absorption centered at $\lambda_{\text{max}} = 450$ nm was also observed in **8**, of which the band extended beyond $\lambda_{\text{max}} = 800$ nm (Figure 2). The UV/Vis spectrum of **9** displayed two-broad absorption centered at $\lambda_{\text{max}} = 583$ nm and $\lambda_{\text{max}} = 808$ nm in dichloromethane. When the solvent was changed to 10% dichloromethane in hexane that possess much lower polarity, these bands showed apparent blue-shift to $\lambda_{\text{max}} = 572$ nm and 753 nm, respectively. These results suggest the intramolecular CT characters of these absorption bands (Figure 3).¹³ The bis-TCNE adduct **12** exhibited a strong and broad CT absorption band at 443 nm and 544 (sh) nm in dichloromethane.

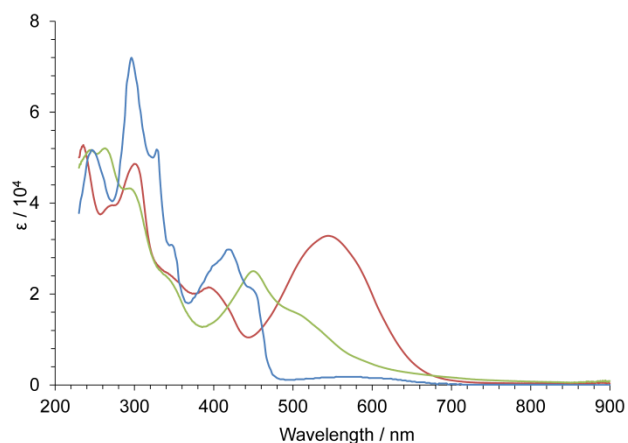


Fig. 2 UV/Vis spectra of **3** (blue line), **7** (red line) and **8** (green line) in dichloromethane.

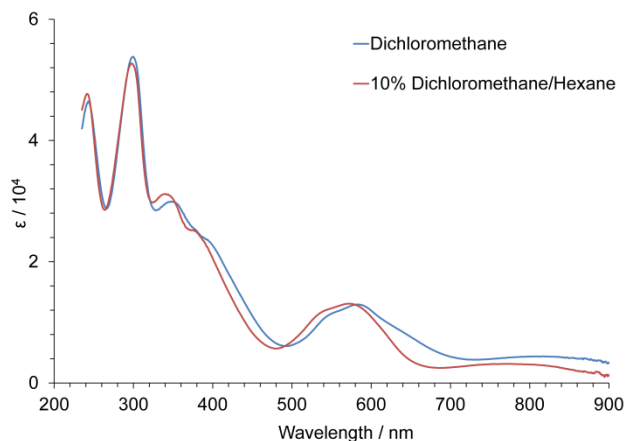


Fig. 3 Solvent dependence for UV/Vis spectra of **9** in dichloromethane (blue line) and 10% dichloromethane/hexane (red line).

The time dependence density functional theory (TD-DFT) calculation was performed for **9''**, in which the isopropyl group was replaced with H group, in order to clarify an origin for broad absorption of **9**.¹⁴ The frontier Kohn–Sham orbitals of **9''** are shown in Figure 4. The broad CT-absorption beyond to near-infrared region of **9''** originated from the HOMO located on azulene-ring to the LUMO that was mainly located on the 6,6-dicyanofulvene moiety. The broad absorption of **9** centered at $\lambda_{\text{max}} = 583$ nm is confirmed that the absorption band arisen from the overlapping of some transition as shown in Table 2.

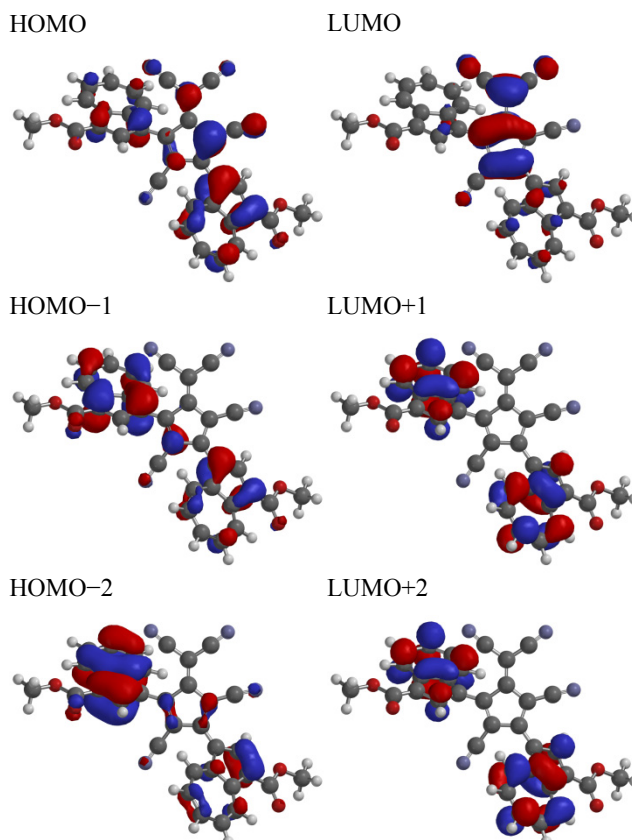


Fig. 4 Frontier Kohn-Sham orbitals of **9''** at the B3LYP/6-31G** level.

Table 2 Electronic transitions for **9**^{••} derived from the computed values based on B3LYP/6-31G** method and experimental values from **9**.

Experimental λ_{\max} (log ϵ)	Computed Value		Composition of band ^{a,b} /CI coefficients ^c
	λ_{\max}	Strength	
808 (3.64)	815	0.0853	H→L/0.94
583 (4.11)	611	0.5618	H-2→L/0.27 H-1→L/0.89
542 sh (4.03)	533	0.0062	H→L+2/0.62
	522	0.0067	H-1→L+1/0.40 H→L+1/0.55
			H→L+2/0.59

^a H = HOMO. ^b L = LUMO. ^c CI = configuration interaction.

5 Electrochemistry

To clarify the electrochemical properties, the redox behavior of **5–9** and **12** was examined by CV and differential pulse voltammetry (DPV). The redox potentials (in volts vs Ag/AgNO₃) of **5–9** and **12** are summarized in Table 3. The cyclic voltammograms of **6**, **8** and **12** are shown in Figures 5, 6 and 7, respectively.

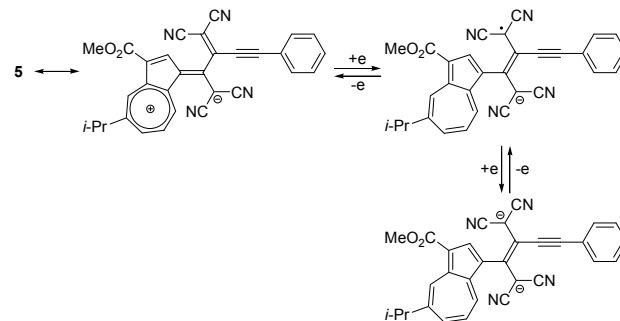
Table 3 Redox potentials^[a] of the compounds **5–9** and **12**.

Sample	Method	E_1^{ox}	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}
5	CV		-0.39	-0.87		
	(DPV)	(+1.87)	(-0.37)	(-0.85)		
6	CV	+0.57	-0.80	-1.08		
	(DPV)	(+0.56)	(-0.78)	(-1.06)		
7	CV		-0.49	-0.90	-1.76	
	(DPV)	(+1.21)	(-0.47)	(-0.88)	(-1.74)	
8	CV		+0.23	-0.37	-1.33	
	(DPV)	(+1.40)	(+0.21)	(-0.35)	(-1.31)	(-1.66)
9	CV		-0.32	-0.59		
	(DPV)	(+0.98)	(-0.30)	(-0.57)	(-1.75)	
12	CV		-0.44	-0.62	-0.99	-1.08
	(DPV)	(+1.35)	(-0.42)	(-0.60)	(-0.97)	(-1.06) ^[b]

^a Redox potentials were measured by CV and DPV [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 Fe/Fe⁺ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.

^b The E_5^{red} and E_6^{red} were observed at -1.88 V and -1.96 V, respectively.

All novel donor–acceptor chromophores **5–9** and **12** showed reversible reduction waves on CV. The TCBD derivative **5** exhibited a reversible two-step reduction wave, of which potentials were identified at -0.39 V and -0.87 V by CV. These results should be attributable to the generation of dianionic species owing to electron acceptance by the TCBD moiety, as illustrated in Scheme 6.



Scheme 6 Presumed electrochemical behavior of **5**.

In the case of the electrochemical analysis of **6**, a reversible one-stage two-electron oxidation wave (+0.57 V) and two-step reduction wave (-0.80 V and -1.08 V) was observed on CV, owing to the redox activities of TCBD and 1,2-bis(1,3-dithiol-2-ylidene)ethane units (Figure 5). The first reduction potential of **6** (-0.80 V) was much more negative than that of **5** (-0.39 V). These results indicate that the 1,2-bis(1,3-dithiol-2-ylidene)ethane substituent on **6** leads to an increase in the LUMO-level of the molecule, due to the strong electron-donating nature of the 1,2-bis(1,3-dithiol-2-ylidene)ethane moiety.

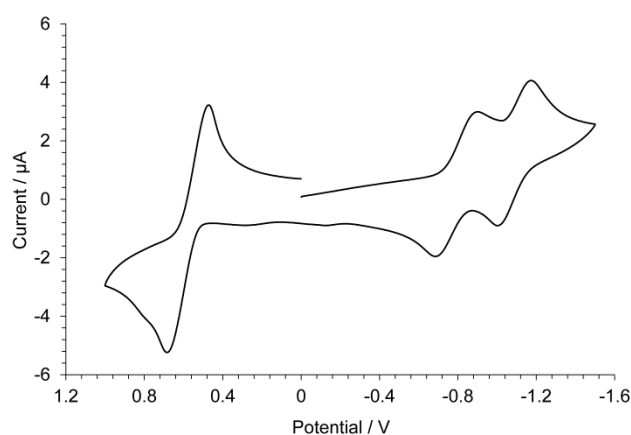


Fig. 5 Cyclic voltammogram of **6** (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate = 100 mVs⁻¹.

The electrochemical reduction of **7** showed a reversible three-stage wave on CV (-0.49 V, -0.90 V and -1.76 V) by the formation up to a trianionic species, which may include the reduction of an azulene ring. The electrochemical reduction of **8** exhibited a reversible three-step reduction wave, whose potentials were identified at +0.21 V, -0.35 V and -1.31 V by DPV, in which the second reduction wave should be concluded to be a two-electron transfer in one step to form a tetraanionic species (Figure 6). The first reduction of **8** (+0.23 V) showed rather less negativity, compared with those of **5** (-0.39 V) and **7** (-0.49 V). Furthermore, the first reduction potential of **8** exhibited the least negative value, compared with those of TCBD and dicyanoquinodimethane (DCNQ) derivatives ever reported.¹⁵ These results indicate that combined two TCBD units in **8** fairly reduce the LUMO-level resulted into the increase of the π -accepting property.

A reversible two-stage wave was also observed in **9** on CV (−0.32 V and −0.59 V), owing to the formation of a dianionic species. The electrochemical reduction of **12** exhibited a reversible four-step reduction wave, the potentials of which were identified at −0.42, −0.60, −0.97 and −1.06 V by DPV, which were attributed to the formation up to a tetraanionic species due to the reduction of the two TCBD moieties (Figure 7).

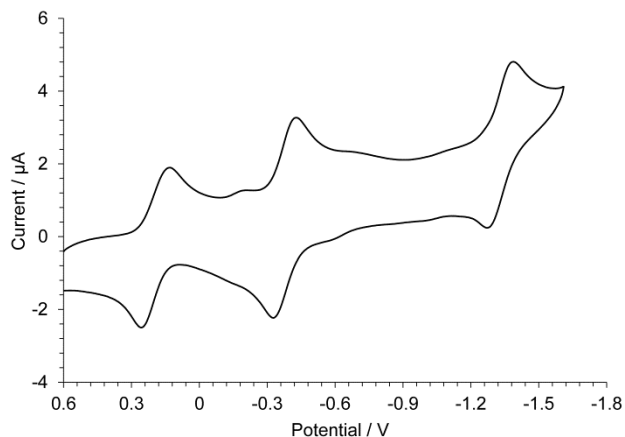


Fig. 6 Cyclic voltammogram of **8** (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{−1}.

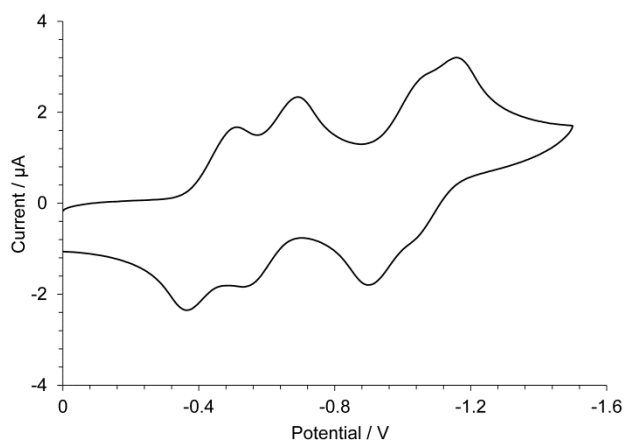


Fig. 7 Cyclic voltammogram of **12** (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{−1}.

Conclusions

In conclusion, azulene-substituted butadiynes **2**, **3** and **4** were prepared by Hay and Glaser reactions, respectively. A series of azulene-substituted TCBD chromophores possessing the acetylene moiety **5** and **7** were synthesized by the [2 + 2] cycloaddition reaction of **2** and **3**, respectively, with TCNE. The [2 + 2] cycloaddition of **5** with TTF gave novel donor–acceptor chromophore **6**. The reaction of **7** with TCNE gave the product **8** with two TCBD moieties and 6,6-dicyanofulvene derivative **9**. Compounds **11** was prepared by the Pd-catalyzed alkynylation of 1,4-diodobenzene with butadiyne **10**, which was prepared by the desilylation of **4**, under Sonogashira–Hagihara conditions. The synthesis of the TCNE/TTF double adduct of **10** was also examined, but the [2 + 2] cycloaddition reaction of **12** with TTF

did not afford the presumed double adduct. An analysis by CV and DPV showed that compound **6** exhibited attractive amphoteric redox properties, owing to the electrochemical oxidation of 1,2-bis(1,3-dithiol-2-ylidene)ethane and reduction of TCBD moieties. It is noteworthy that the first reduction potential of **8** with two TCBD moieties exhibited the least negative value, compared with those of TCBD and DCNQ derivatives ever reported. Construction of reversible multistage redox systems based on the donor–acceptor system is currently examined in our laboratory.

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