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PAPER

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

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

Introduction

Tetrathiafulvalene (TTF) is well known as a powerful electron donor to form charge-transfer (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]

Hopf *et al.* reported the [2 + 2] cycloaddition reaction of TTF, a strong electron donor, with electron-deficient acetylenes bearing a dicyanoethylene substituent to afford 1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives with a dicyanoethylene substituent.[2] As an extension of this study, Diederich *et al.* reported the sequential [2 + 2] cycloaddition reaction of tetracyanoethylene (TCNE) and TTF with dialkylamino- (DAA-) substituted electron-rich butadiynes yielding multivalent 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 ($C_{10}H_8$) has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.[4] Recently, we 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-meditated oxidative coupling under Eglinton conditions.[6] Although 1-azulenylbutadiynes are promising building blocks for the construction of novel CT chromophores, reactivity of their derivatives has not been energetically investigated so far. Similar to the DAA-substituent, the 1-position of an azulene ring possesses strong electron-donating properties with high reactivity toward electrophilic substitution reactions. Thus, butadiyne derivatives substituted by a 1-azulenyl moiety should be expected to afford a new series of donor–acceptor chromophores by sequential [2 + 2] cycloaddition reactions with TCNE and TTF. Furthermore, azulene-substituted donor–acceptor chromophores may exhibit multistage amphoteric redox behaviour with a 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 the spectroscopic and electrochemical properties of the novel donor–acceptor chromophores clarified by UV/Vis spectroscopy and electrochemical analysis.

Results and discussion

Synthesis

Preparation of azulene-substituted butadiene derivatives, *i.e.*, methyl 7-isopropyl-3-(4-phenylbuta-1,3-diynyl)azulene-1-carboxylate (**2**), 1,4-bis(7-isopropyl-1-methoxycarbonylazulen-3-yl)-buta-1,3-diyne (**3**), and methyl 7-isopropyl-3-(4-trimethylsilyl-buta-1,3-diynyl)azulene-1-carboxylate (**4**), was investigated by Cu-mediated Hay[7] cross- and Glaser[8] 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

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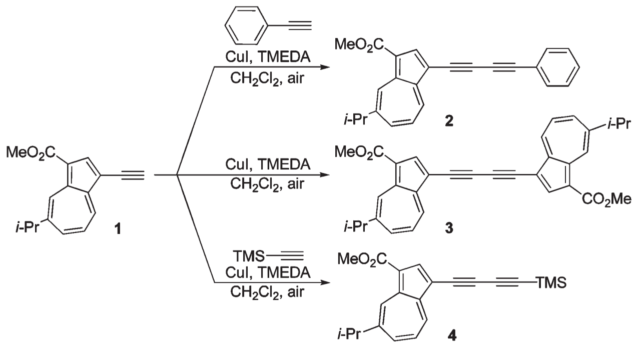
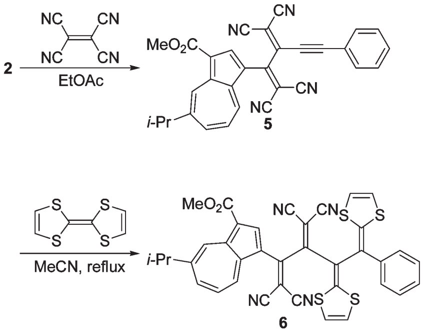


Scheme 1 Synthesis of 1-azulenylbutadiynes **2**, **3** and **4**.

(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 similar reaction conditions. Similar to 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 show 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.

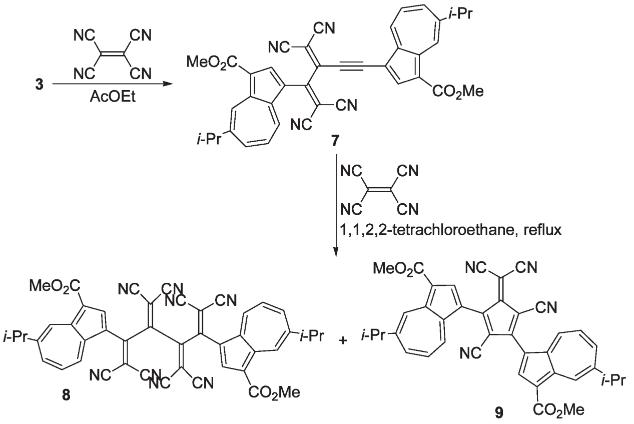
The sequential [2 + 2] cycloaddition reaction of **2** and **3** with TCNE and TTF was examined for the construction of novel donor–acceptor chromophores. Thus, the reaction of **2** with TCNE was examined in ethyl acetate at room temperature to yield **5** in 95% yield.[3,5,9] Subsequent [2 + 2] cycloaddition reaction of the remaining ethynyl moiety of **5**, contiguous to the phenyl group, with excess TCNE did not proceed even under reflux conditions in DMF. These results indicate the low reactivity of the $C\equiv C$ 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 an 84% yield in each step. However, the cascade reaction requires a tedious separation process.



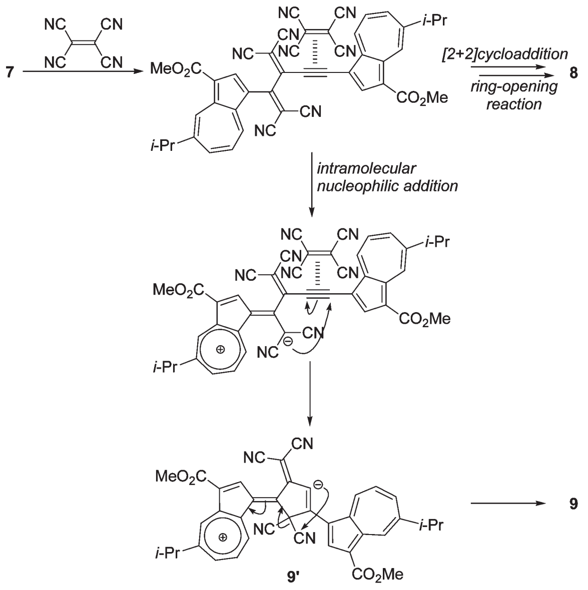
Scheme 2

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 resulted in the recovery of the TCBD **7**. Meanwhile, the subsequent [2 + 2] cycloaddition of **7** with TCNE was observed under reflux conditions in 1,1,2,2-tetrachloroethane to afford the double TCNE-adduct **8** in 71% yield, along with the novel 6,6-dicyanofulvene derivative **9** in 22% yield (Scheme 3).

When compounds **7** and **8** were refluxed in 1,1,2,2-tetrachloroethane without TCNE, 6,6-dicyanofulvene **9** could not be obtained, but resulted in the recovery of the starting compounds **7** and **8**. Thus, TCNE has an important role in the formation of the 6,6-dicyanofulvene derivative **9**. The presumed reaction mechanism for the formation of **8** and **9** is illustrated in Scheme 4. This reaction involves two reaction pathways to afford **8** and **9**. Initially, TCNE exhibits coordination to **7** with the electron-rich acetylene moiety attached to the 1-azulenyl group. In one pathway, the TCNE molecule undergoes a [2 + 2]



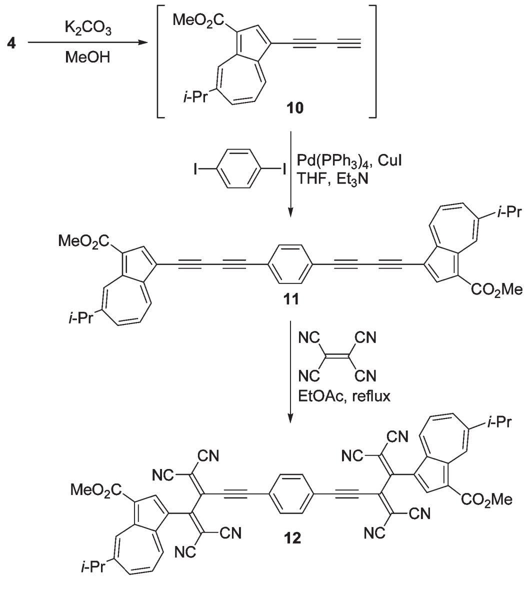
Scheme 3



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

cycloaddition with the acetylene moiety of **7** to afford the cyclobutene intermediate. The 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 due to conjugation with the 1-azulenyl group, attacks the intramolecular acetylene moiety with a decreased LUMO-level because of the TCNE coordination, to form the five-membered ring of **9′**. In the generated zwitterionic species **9′**, the migration of a cyano group results in the formation of 6,6-dicyanofulvene derivative **9**.[11] Recently, Diederich *et al.* reported the first synthesis of donor-substituted 6,6-dicyanofulvene derivatives with interesting optoelectronic properties.[12] In the view point of azulene chemistry, compound **9** is the first example of a 6,6′-dicyanofulvene derivative with an azulene ring substituent.

Compound **11** was prepared by the Pd-catalyzed alkynylation 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 for employment in further transformations. The cross-coupling reaction of **10** with 1,4-diiodobenzene using $Pd(PPh_3)_4$ as a catalyst, and the subsequent chromatographic purification of the reaction mixture on silica gel, afforded the desired **11** in 87% yield. Similar to the results for the butadiynes **2** and **3**, the reaction of **11** with TCNE afforded the bis-adduct **12** in 95% yield. Regarding the synthesis of the TCNE/TTF double adduct, the [2 + 2] cycloaddition reaction of **12** with TTF was also examined under similar conditions used for the preparation of **6**. However, in contrast to the results for 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

Table 1 Absorption maxima [nm] and their coefficients (log ε) of compounds **5–9**, and **12** in dichloromethane and in 10% CH_2Cl_2–hexane

Sample	λ_{max} (log ε) in CH_2Cl_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.

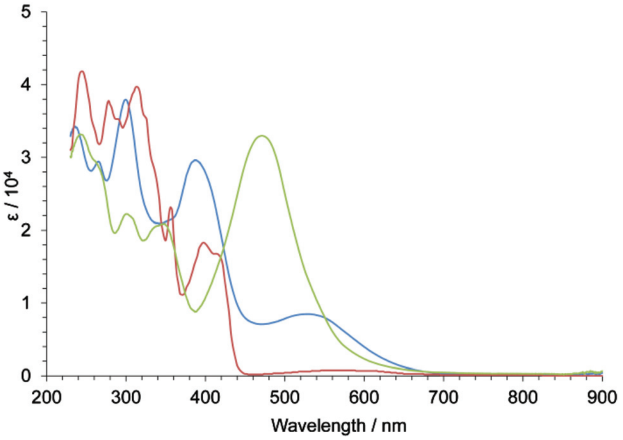


Fig. 1 UV/Vis spectra of **2** (red line), **5** (blue line) and **6** (green line) in dichloromethane.

Spectroscopic properties

The structures of these novel compounds **2–12** were confirmed by spectral data including ^1H, ^{13}C 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.

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

Compound **7** exhibits two CT absorption bands at λ_{max} = 394 nm (weak) and λ_{max} = 545 nm (strong) in dichloromethane (Fig. 2). The longest absorption of **7** displays a bathochromic shift of 15 nm compared with that of **5** (λ_{max} = 530 nm). These results indicate that the π-conjugation is efficiently expanded by

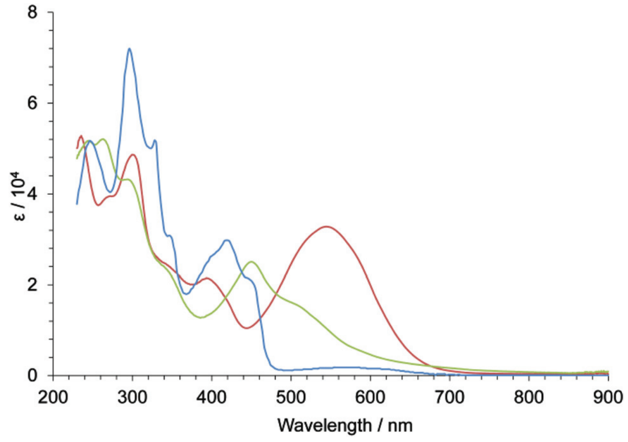


Fig. 2 UV/Vis spectra of **3** (blue line), **7** (red line) and **8** (green line) in dichloromethane.

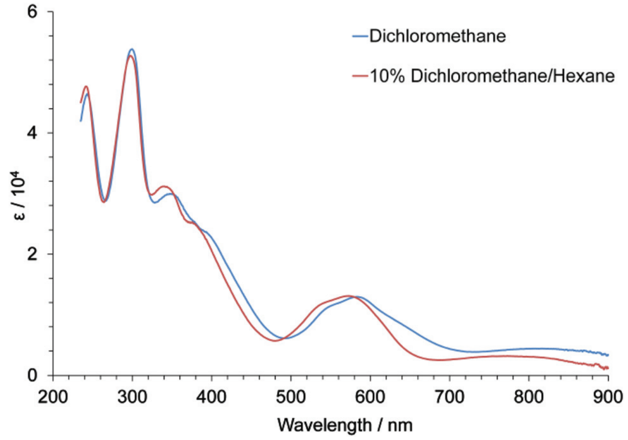


Fig. 3 Solvent dependence of the UV/Vis spectra of **9** in dichloromethane (blue line) and 10% dichloromethane–hexane (red line).

the 1-azulenyl group substituent rather than the phenyl group substituent. A broad CT absorption centered at λ_{max} = 450 nm and extending beyond λ_{max} = 800 nm was also observed in **8** (Fig. 2). The UV/Vis spectrum of **9** displays two broad absorptions centered at λ_{max} = 583 nm and λ_{max} = 808 nm in dichloromethane. When the solvent was changed to 10% dichloromethane in hexane, which possesses a much lower polarity, these bands showed an apparent blue-shift to λ_{max} = 572 nm and 753 nm, respectively. These results suggest the intramolecular CT character of these absorption bands (Fig. 3).[13] The bis-TCNE adduct **12** exhibits strong and broad CT absorption bands at 443 nm and 544 (sh) nm in dichloromethane.

The time dependence density functional theory (TD-DFT) calculation was performed for **9″**, in which the isopropyl groups were replaced with H groups, in order to clarify the origin of the broad absorption for **9**.[14] The frontier Kohn–Sham orbitals of **9″** are shown in Fig. 4. The broad CT-absorption beyond the near-infrared region for **9″** originated from the overlap of the HOMO located on the azulene-ring with the LUMO that was mainly located on the 6,6-dicyanofulvene moiety. The broad absorption of **9** centered at λ_{max} = 583 nm was confirmed to arise from the overlap of some transitions as shown in Table 2.

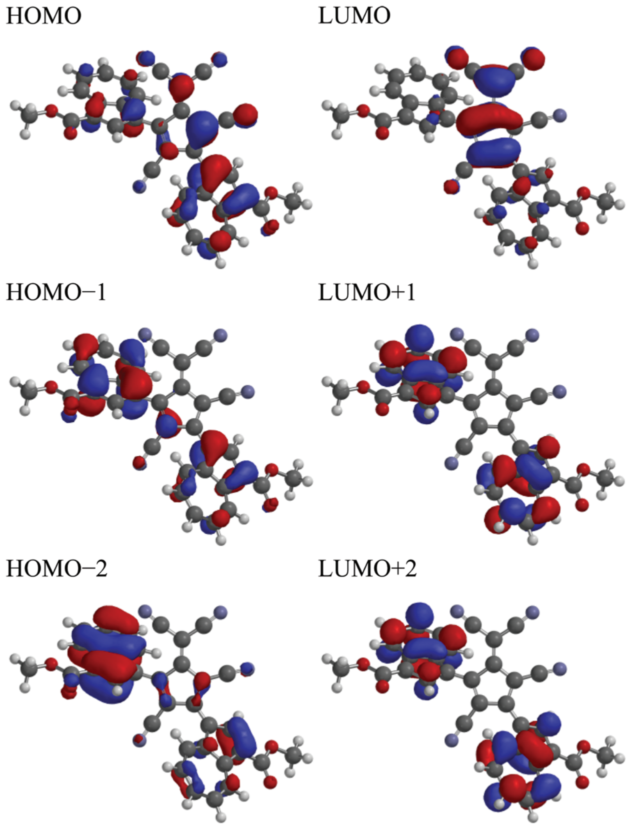


Fig. 4 Frontier Kohn–Sham orbitals of **9″** at the B3LYP/6-31G** level.

Table 2 Electronic transitions for **9″** derived from the computed values based on the 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.

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/$AgNO_3$) of **5–9** and **12** are summarized in Table 3. The cyclic voltammograms of **6**, **8** and **12** are shown in Fig. 5–7, respectively.

All the novel donor–acceptor chromophores **5–9** and **12** showed reversible reduction waves in 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 could be attributable to the generation of a dianionic

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/AgNO$_3$, 1 mM in benzonitrile containing Et$_4$NClO$_4$ (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mV s^{-1}, and Fc/Fc$^+$ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses. [b] The E_5^{red} and E_6^{red} were observed at −1.88 V and −1.96 V, respectively.

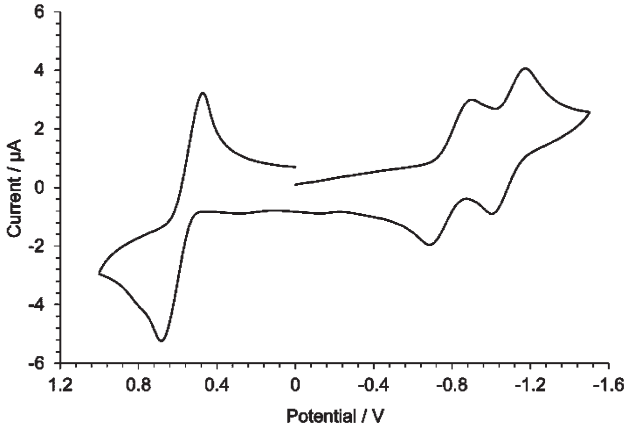


Fig. 5 Cyclic voltammogram of **6** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

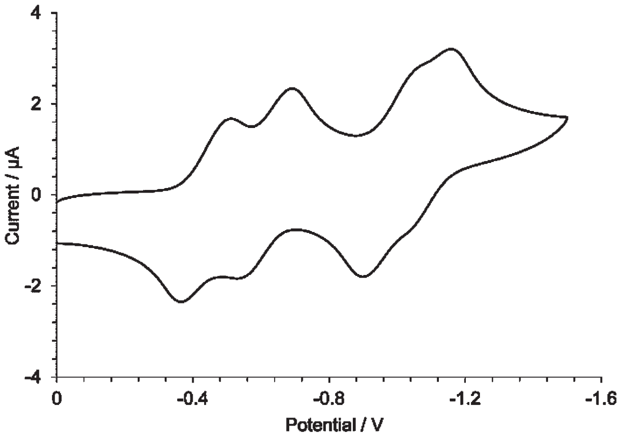


Fig. 7 Cyclic voltammogram of **12** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

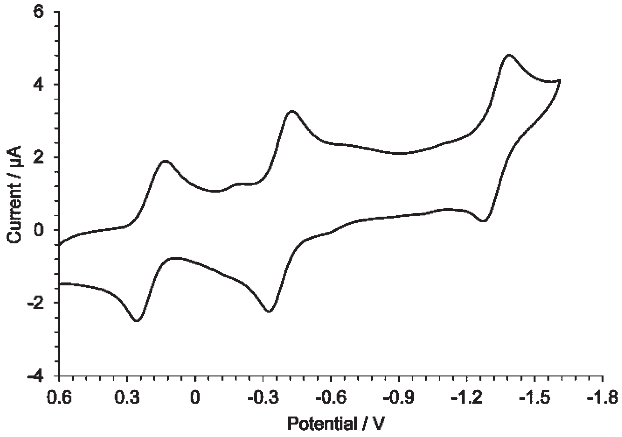
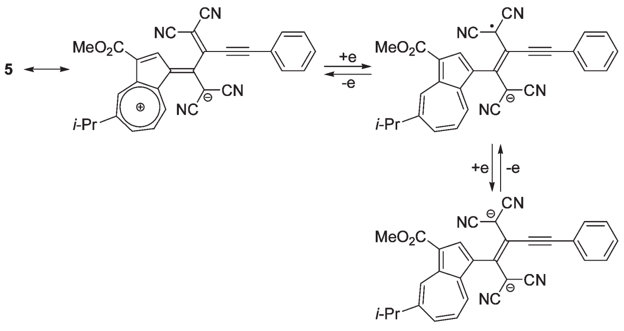


Fig. 6 Cyclic voltammogram of **8** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.



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

species owing to electron acceptance by the TCBD moiety, as illustrated in Scheme 6.

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 in CV, owing to the redox activities of the TCBD and 1,2-bis(1,3-dithiol-2-ylidene)ethane units (Fig. 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.

The electrochemical reduction of **7** showed a reversible three-stage wave in CV (−0.49 V, −0.90 V and −1.76 V) by the formation of 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 could be concluded to be a two-electron transfer in one step to form a tetraanionic species (Fig. 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 previously reported for TCBD and dicyanoquinodimethane (DCNQ) derivatives.[15] These results indicate that the combined two TCBD units in **8** fairly reduce the LUMO-level resulting in the increase of the π-accepting property.

A reversible two-stage wave was also observed in **9** in 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 of up to a tetraanionic species due to the reduction of the two TCBD moieties (Fig. 7).

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 an 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 the novel donor–acceptor chromophore **6**. The reaction of **7** with TCNE gave the product **8** with two TCBD moieties and the 6,6-dicyanofulvene derivative **9**. Compound **11** was prepared by the Pd-catalyzed alkynylation of 1,4-diiodobenzene 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 the 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 previously reported. Construction of reversible multistage redox systems based on the donor–acceptor system is currently being examined in our laboratory.

Acknowledgements

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