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Reactions between 1-Ethynylazulenes and 7,7,8,8-Tetracyanoquinodimethane (TCNQ): Preparation, Properties, and Redox Behavior of Novel Azulene-Substituted Redox-Active Chromophores

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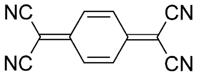
[2+2] Cycloaddition/cycloreversion reactions between TCNQ and mono- or bis[2-(azulen-1-yl)ethynyl]benzene or -thiophene derivatives were examined: the corresponding TCNQ adducts, novel azulene-substituted redox-active chromophores, were produced in excellent yields. TCNE/TCNQ double adducts were also prepared both by stepwise and by one-pot cascade reactions. The redox behavior of these novel azulene-substituted chromophores was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Significant color changes in these azulene-substituted chromophores under electrochemical reduction conditions were observed by visible spectroscopy.

Introduction

The powerful electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) is well known to form a variety of intermolecular charge-transfer (CT) complexes with various electron donors.[1]



7,7,8,8-Tetracyanoquinodimethane (TCNQ)

Recently, Diederich et al. reported reactions between TCNQ and a variety of *N*,*N*-dialkylaniline-substituted (DAA-substituted) alkynes to afford [2+2] cycloaddition products as a novel type of CT chromophores in excellent yields.[2] They also reported that the chromophores exhibit optoelectronic and redox properties. These CT chromophores would be expected to show optical nonlinearities and could be utilizable as organic-based magnets and conductive materials.[3]

Azulene ($C_{10}H_8$) has attracted the interest of many research groups as a result of its unusual properties, as well as its beautiful blue color.[4] Recently we have reported reactions between tetracyanoethylene (TCNE) and mono-, bis-, and tris[2-(azulen-1-yl)ethynyl]benzene and -thiophene derivatives, giving the corresponding [1,1,4,4-tetracyano-2-(azulen-1-yl)-3-butadienyl] chromophores.[5] These new chromophores exhibit multistep reduction waves upon cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Moreover, significant multistep color changes are also observed on their electrochemical reduction.

Reactions between TCNQ and 1-ethynylazulene derivatives, however, have never been examined. As in their reactions with TCNE, 1-ethynylazulene derivatives should react with TCNQ to afford novel azulene-substituted redox-active chromophores. Moreover, the new azulene-substituted TCNQ adducts should exhibit multistep redox activities, and significant color changes should be observed under electrochemical reaction conditions, as in the case of [1,1,4,4-tetracyano-2-(azulen-1-yl)-3-butadienyl] chromophores.

Here we describe [2+2] cycloaddition/cycloreversion reactions between TCNQ and mono- and bis[2-(azulen-1-yl)ethynyl]benzene and -thiophene derivatives. The electronic properties of these novel redox-active chromophores are characterized by electrochemical analysis and absorption spectroscopy.

Results and Discussion

Synthesis

The mono- and bis[2-(azulen-1-yl)ethynyl]benzene and -thiophene derivatives **1**–**4** were prepared by Sonogashira–

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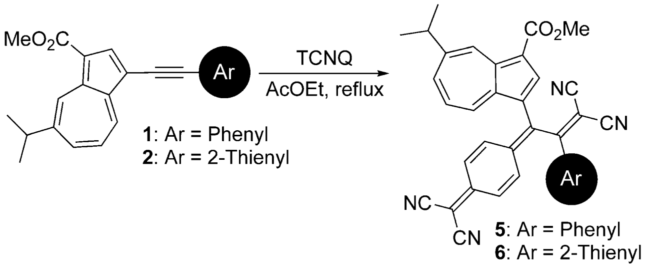
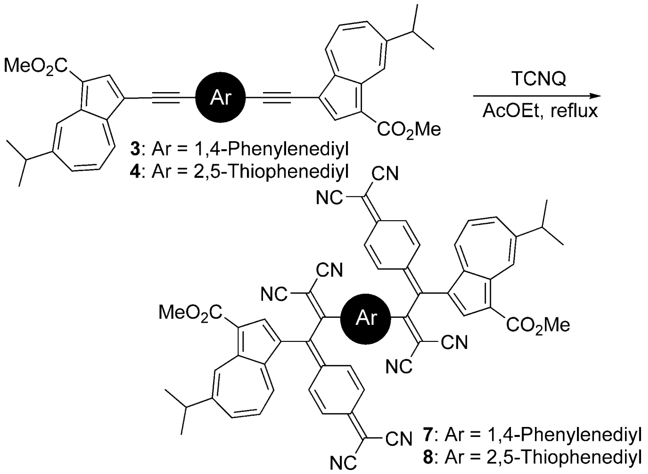
Hagihara reactions according to the procedure reported by us recently.[5] The novel redox-active chromophores **5**–**8** were then obtained through [2+2] cycloaddition/cycloreversion reactions between **1**–**4** and TCNQ, as in the procedure reported by Diederich et al.[2] Treatment of **1** with TCNQ in ethyl acetate at reflux yielded the presumed **5** in 96% yield. Likewise, treatment of **2** with TCNQ afforded **6** in 93% yield (Scheme 1). Like the reaction with TCNE, this readily proceeded under relatively mild conditions, despite the electron-withdrawing group (methoxycarbonyl) substituted on the azulene ring. The high reactivity should be attributed to the highly electron-donating properties of the azulene ring at the 1-position.



Scheme 1.

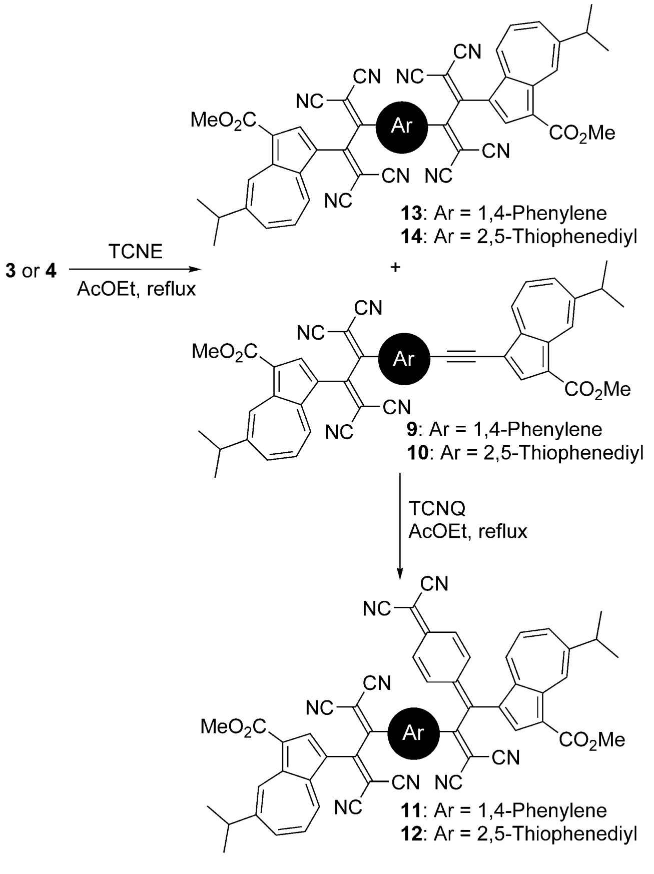
Similarly to the results with the monosubstituted benzene and thiophene derivatives, treatment of the bis[2-(azulen-1-yl)ethynyl] derivatives **3** and **4** with TCNQ afforded the novel double-substituted chromophores **7** and **8** in 94% and 92% yields, respectively (Scheme 2).



Scheme 2.

Recently, Diederich and co-workers have reported one-pot cascade reactions with TCNE, TTF, and diacetylenes for the construction of novel multivalent charge-transfer chromophores.[6] However, cascade reactions with TCNE, TCNQ, and bisalkynes had never been reported. We thus investigated the preparation of the TCNE/TCNQ double adducts **11** and **12** as novel multivalent charge-transfer chromophores both by stepwise and also by one-pot cascade reactions of **3** and **4** with TCNE and TCNQ in order to explore their physical and electrochemical properties.

Treatment of **3** with TCNE gave the mono adduct **9** in 88% yield, along with **13**[5] in 4% yield (Scheme 3).[7] The synthesis of the TCNE/TCNQ double adduct **11** was achieved in 84% yield by treatment of **9** with TCNQ (Scheme 3). The one-pot cascade reaction of **3** with TCNE and TCNQ gave **11** in 30% yield, which corresponds to a yield of 55% per step, along with **7** (29%) and **13** (32%). However, the cascade reaction required a tedious separation process.



Scheme 3.

Likewise, treatment of **4** with TCNE afforded **10** in 88% yield, along with **14**[5] in 5% yield (Scheme 3). The resulting mono adduct **10** was treated with TCNQ to give the TCNE/TCNQ double adduct **12**, with a thiophene core, in 85% yield. The one-pot cascade reaction of **4** with TCNE and TCNQ also afforded **12** in 30% yield, corresponding to a yield of 55% per step, along with **8** (27%) and **14** (34%). These new azulene-substituted chromophores **5** and **6** and the multivalent charge-transfer chromophores **7**, **8**, **11**, and **12** are stable, deep-colored crystals and, like the [1,1,4,4-tetracyano-2-(azulen-1-yl)-3-butadienyl] chromophores, are storable in the crystalline state at room temperature.

Spectroscopic Properties

Compounds **5**–**12** were fully characterized by their spectroscopic data, as shown in the Supporting Information. The reported NMR assignments were confirmed by experiments such as the HMQC, HMBC, and NOE techniques. The mass spectra of **5**–**12** ionized by ESI showed the correct molecular ion peaks. The characteristic stretching-vibration band of the C≡N group was observed at 2220 to 2208 cm^{-1} in the IR spectra of **5**–**12**. These results are consistent with the structures of these products.

UV/Vis spectra of **5**–**12** in CH_2Cl_2 and in hexane are shown in the Supporting Information. Their absorption maxima and coefficients (logε) are summarized in Table 1. As would be expected from their structures, the TCNQ adducts **5**–**8**, **11**, and **12** showed characteristic CT absorptions in the visible region and solvatochromism was also observed. Compound **5** exhibited weak and strong absorptions at λ_{max} = 393 and 641 nm in CH_2Cl_2, and the largest solvent effect was observed when the solvent was changed from CH_2Cl_2 to hexane (λ_{max} = 598 nm). Compound **6** exhibited a strong CT absorption at λ_{max} = 626 nm in CH_2Cl_2, and a hypsochromic shift of 31 nm was observed upon the measurement in hexane (Figure 1).

Table 1. Absorption maxima [nm] and coefficients (logε) of **5**–**8**, **11**, and **12** in dichloromethane and in hexane.

Sample	λ_{max} (logε) CH_2Cl_2	hexane
5	393 (4.26), 641 (4.43)	391 (4.28), 598 (4.42)
6	362 (4.40), 626 (4.47)	362 sh (4.39), 595 (4.48)
7	358 sh (4.75), 627 (4.70)	380 sh (4.48), 636 (4.46)
8	391 (4.67), 590 (4.69)	388 (4.39), 574 (4.39)
11	432 (4.90), 586 (4.64)	411 (4.89), 566 (4.62)
12	432 (4.73), 586 (4.46)	418 (4.69), 562 (4.43)

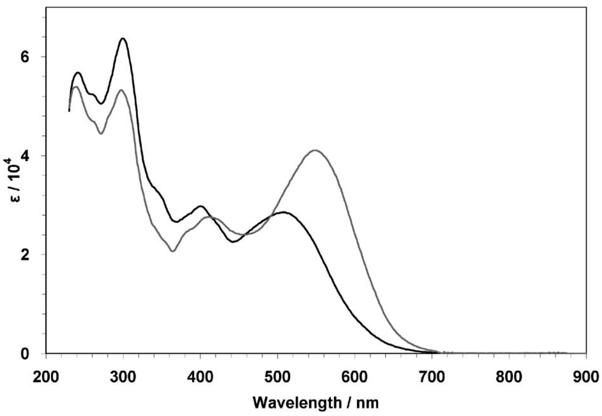


Figure 1. UV/Vis spectra of **5** (black line) and **6** (gray line) in dichloromethane.

Compound **7** exhibited a strong CT absorption at λ_{max} = 627 nm in CH_2Cl_2. Inconsistently with the expansion of the π-conjugation, the CT absorption of **7** showed a hypsochromic shift of 14 nm relative to **5**. When the solvent of **7** was changed to hexane, the CT absorption maximum exhibited a bathochromic shift of 9 nm, but the broad absorption band now reached into the near-infrared region. Two absorption bands were observed for **8** in all solvents, and a hypsochromic shift was again observed on changing the solvent to hexane (Figure 2).

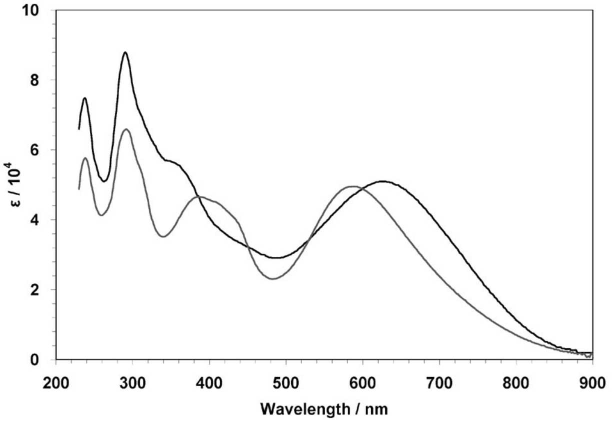


Figure 2. UV/Vis spectra of **7** (black line) and **8** (gray line) in dichloromethane.

Compound **11** in CH_2Cl_2 exhibited two strong absorptions at λ_{max} = 432 and λ_{max} = 586 nm corresponding to the dual chromophores. The solvent effect was also observed, with the two CT absorptions showing hypsochromic shifts of 21 nm and 20 nm, respectively, with a change in the solvent to hexane. Two CT absorptions were also observed for **12** in CH_2Cl_2, at λ_{max} = 432 nm and λ_{max} = 586 nm (Figure 3). The largest solvent effect was observed (see Supporting Information) when the solvent was changed from $CHCl_3$ (λ_{max} = 588 nm) to hexane (λ_{max} = 562 nm).

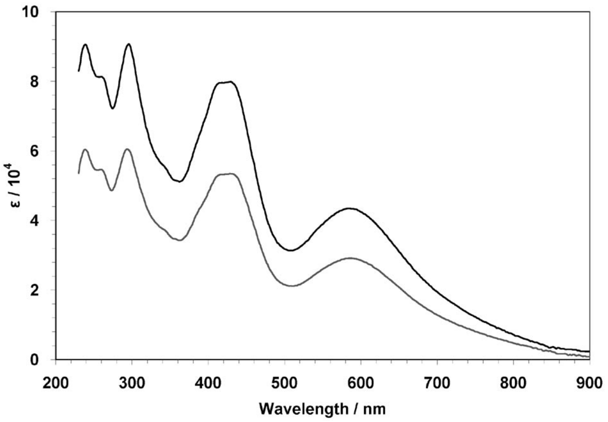


Figure 3. UV/Vis spectra of **11** (black line) and **12** (gray line) in dichloromethane.

Redox Potentials

To clarify their electrochemical properties, the redox behavior of **5**–**12** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Measurements were made with use of a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte with platinum wire auxiliary and working electrodes. All measurements were carried out under argon, and potentials were related to the reference electrode formed by Ag/Ag^+ with use of Fc/Fc^+, which discharges at +0.15 V, as internal reference. The redox potentials of **5**–**12** (in volts vs. Ag/AgNO$_3$) are summarized in Table 2.

Table 2. Redox potentials[a] of **5**–**14**.

Sample	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]	E_4^{red} [V]	E_5^{red} [V]
5	–0.43	–0.59			
	(–0.41)	(–0.58)	(–0.90)	(–1.93)	
6	–0.44	–0.58			
	(–0.46)	(–0.57)	(–1.91)	(–2.03)	
7	–0.38 (2e)	–0.55 (2e)			
	(–0.38)	(–0.55)	(–1.93)	(–2.16)	
8	–0.31	–0.43	–0.61 (2e)	–1.90	
	(–0.31)	(–0.41)	(–0.59)	(–1.88)	(–2.15)
9	–0.57	–0.98	–1.62	–1.94	
	(–0.56)	(–0.96)	(–1.61)	(–1.92)	(–2.16)
10	–0.61	–0.92	–1.62	–1.88	
	(–0.59)	(–0.89)	(–1.60)	(–1.86)	(–2.16)
11	–0.32	–0.41	–0.77	–1.00	–1.96
	(–0.30)	(–0.39)	(–0.75)	(–0.98)	(–1.94)
12	–0.32	–0.40	–0.77	–0.99	–1.95
	(–0.30)	(–0.38)	(–0.75)	(–0.97)	(–1.93)
13[5]	–0.46	–0.64	–1.01	–1.11	
	(–0.45)	(–0.63)	(–1.00)	(–1.09)	(–1.90)
14[5]	–0.31	–0.54	–1.10 (2e)		
	(–0.29)	(–0.52)	(–1.09)	(–1.89)	(–2.15)

[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 mVs^{-1}, and Fc/Fc$^+$ = +0.15 V]. In cases of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.

Electrochemical reduction of **5** showed a reversible two-step wave at the half-wave potentials of –0.44 V and –0.59 V upon CV, probably due to the formation of a radical anionic and a dianionic species, respectively (Figure 4). The electrochemical reduction of **5** also exhibited irreversible waves at –0.90 V, –1.93 V, and –2.14 V upon DPV, probably due to the reduction of the substituted azulene moiety.

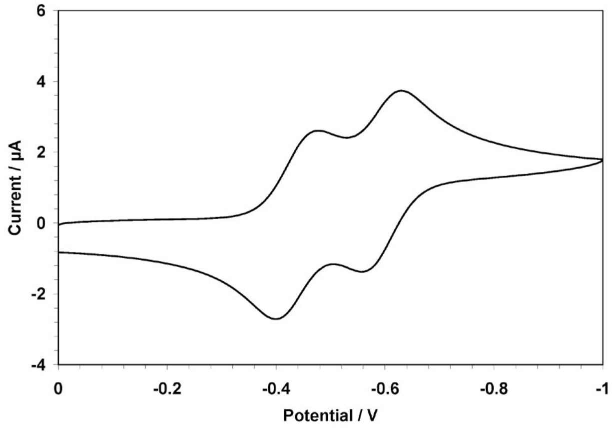


Figure 4. Cyclic voltammograms for the reduction of **5** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate: 100 mV s^{-1}.

The electrochemical reduction of **6** also showed a reversible two-step reduction wave upon CV at –0.44 V and –0.58 V, due to the formation of up to dianionic species.

The bis adduct **7** exhibited a reversible two-step reduction wave attributable to two-electron transfer in each step, the potentials of which were identified by DPV as –0.38 V and –0.55 V, to form dianionic and tetraanionic species, respectively. A reversible four-step wave was observed in **8** upon CV at –0.31 V, –0.43 V, –0.61 V, and –1.94 V, in which the third reduction wave should be regarded as two-electron transfer in one step to form up to pentaanionic species (Figure 5).

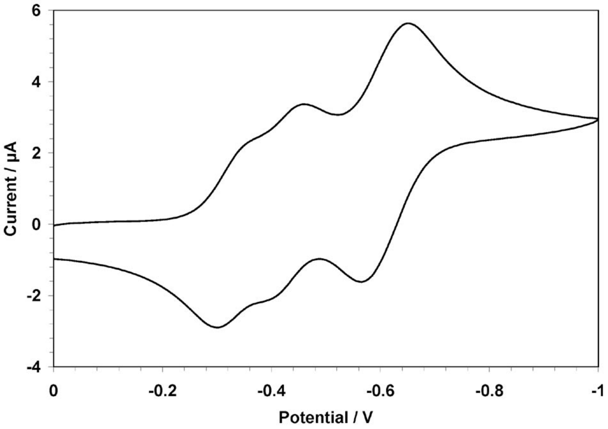


Figure 5. Cyclic voltammograms for the reduction of **8** (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate: 100 mV s^{-1}.

The first reduction potentials of **7** and **8** were less negative than those of **5** and **6**. This indicates that increasing the number of the azulene-substituted chromophores reduces the LUMO levels and enhances their π-accepting properties. Recently, we have reported the redox behavior of compounds **13** and **14** (Scheme 3), which exhibit reversible multistep reduction waves.[3] The first reduction potentials of compounds **7** and **8** are very similar to those of **13** and **14** (**13**: E_1^{red} = –0.46 V; **14**: E_1^{red} = –0.31 V). These results indicated that these novel azulene-substituted chromophores have π-accepting abilities comparable to those of the [1,1,4,4-tetracyano-2-(azulen-1-yl)-3-butadienyl] chromophores **13** and **14**.

The redox behavior of the TCNE/TCNQ double adducts **11** and **12** was also examined. Electrochemical reduction of **11** showed a reversible five-step reduction wave at the half-wave potentials of –0.32 V, –0.41 V, –0.77 V, –1.00 V, and –1.96 V upon CV, probably due to the formation of up to a pentaanionic species including reduction of the substituted azulene moieties (Figure 6). The TCNE/TCNQ double adduct **12** with a thiophene core also exhibited a reversible five-step reduction wave, the potentials of which were identified at –0.32 V, –0.40 V, –0.77 V, –0.99 V, and –1.96 V upon CV, owing to the formation of up to a pentaanionic species. The first reduction potentials of **11** and **12** were comparable with those of **7** and **8**, so the first reduction wave might be attributable to the reduction of the dicyanoquinodimethane moieties in **11** and **12**.

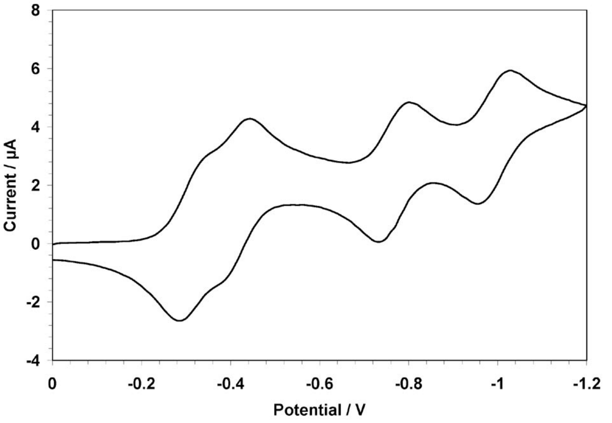


Figure 6. Cyclic voltammograms for the reduction of **11** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate: 100 mV s^{-1}.

The oxidation of these compounds produced voltammograms that were characterized by irreversible waves, probably due to the oxidation of the substituted azulene rings to form unstable radical cationic species.

Electrochromic Analysis

To examine the color changes during the electrochemical reactions, the spectral changes of compounds **5**–**8**, **11**, and **12** were monitored by visible spectroscopy. Constant-current reduction was applied to solutions of **5**–**8**, **11**, and **12**, with a platinum mesh as the working electrode and a wire counter electrode, and visible spectra were measured in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte at room temperature under electrochemical reduction conditions (see the Supporting Information).

The longest-wavelength absorption of **5**, at λ_{max} = 650 nm, gradually decreased and the color of the solution changed from green to orange during the electrochemical reduction. The green color of the solution of **6** also changed to orange during the electrochemical reduction. These changes were accompanied by increases in the broad absorption bands up to the near-infrared region. Reverse oxidation of these orange-colored solutions regenerated the visible spectra of the green-colored **5** and **6**, but incompletely, although good reversibility had been observed upon CV.

When the UV/Vis spectra of **7** were measured under electrochemical reduction conditions, the absorption of **7** at λ_{max} = 648 nm in the visible region also gradually decreased, with increment of a new absorption in the near-infrared region (Figure 7). The absorption bands of **8** in the visible region also gradually disappeared during the electrochemical reduction. The color of the solution gradually changed from deep green to yellow during the electrochemical reduction. Reverse oxidation regenerated the absorptions of **7** and **8**, but again incompletely. The low reversibility for the reduction of **7** and **8** indicates instability of the presumed closed-shell dianionic and tetraanionic species produced by electrochemical reduction under the conditions of the spectral measurements.

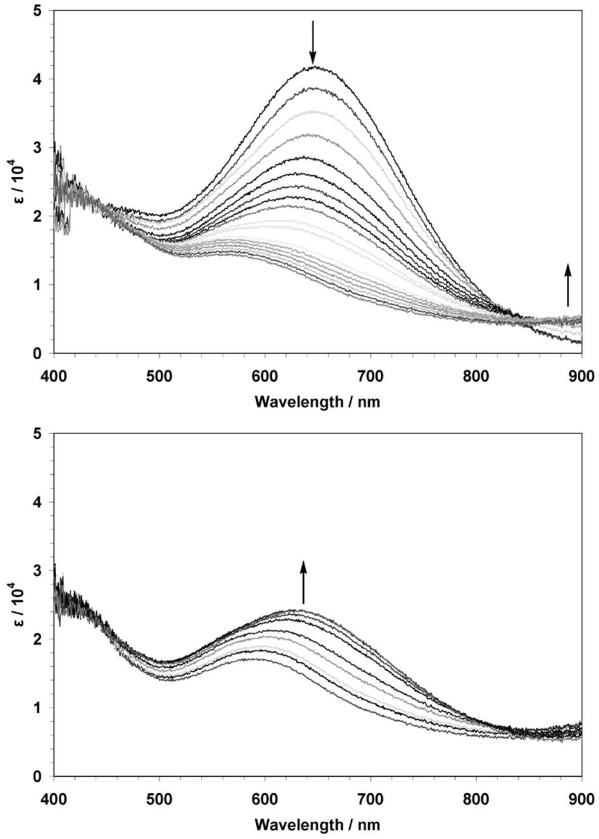


Figure 7. Continuous change in visible spectra of **7** in benzonitrile containing Et_4NClO_4 (0.1 M): constant-current electrochemical reduction (50 uA) at 30 sec intervals (top) and reverse oxidation (bottom) of the reduced species (50 uA) at 30 sec intervals.

We have recently reported the redox behavior of **14**, which exhibited a two-step reversible color change under electrochemical reduction, with rather high reversibility. It therefore appears that the dicyanoquinodimethane structures in **7** and **8** stabilize the reduced species less than is the case in **14**. The UV/Vis spectra of the TCNE/TCNQ double adducts **11** and **12** also showed color changes from green to yellow, and the reverse oxidation of the yellow-colored solutions also regenerated the visible spectra of the green-colored **11** and **12**, but incompletely.

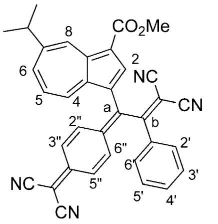
Conclusions

In summary, novel azulene-substituted redox-active chromophores **5**–**8** were prepared in excellent yields through the reactions between TCNQ and the 1-ethynylazulene derivatives **3** and **4** . The TCNE/TCNQ double adducts **11** and **12** were also prepared both by stepwise and also by one-pot cascade reactions with TCNE and TCNQ. Analysis by CV and DPV showed that these compounds **5**–**8**, **11**, and **12** exhibit multistep reduction properties. Moreover, significant color changes were observed during the electrochemical reduction. In attempts to improve the electrochromic properties, preparation of novel azulene-substituted multivalent charge-transfer chromophores with different π-electron cores is now in progress in our laboratory.

Experimental Section

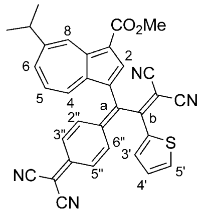
General: For general and electrochemical measurement details see the Supporting Information. Assignment of peaks in the ^{1}H NMR spectra was accomplished by decoupling, NOE, and/or COSY experiments.

{4-[3,3-Dicyano-1-[5-isopropyl-3-(methoxycarbonyl)azulen-1-yl]-2-phenylprop-2-en-1-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (5)



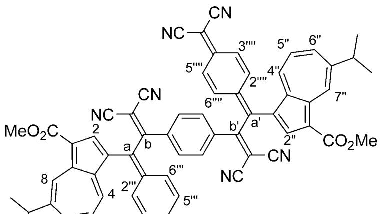
TCNQ (153 mg, 0.75 mmol) was added to a solution of **1** (164 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux for 2 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and Bio-Beads with CH_2Cl_2 to give **5** (256 mg, 96%); m.p. 127.0–132.0 °C (AcOEt). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.90 (s, 1 H, 8-H), 8.29 (d, J = 10.0 Hz, 1 H, 4-H), 8.19 (s, 1 H, H_2), 8.00 (d, J = 10.0 Hz, 1 H, 6-H), 7.71 (d, J = 5.6 Hz, 2 H, 2′-, 6′-H), 7.67 (dd, J = 10.0, 10.0 Hz, 1 H, 5-H), 7.56 (t, J = 5.6 Hz, 1 H, 4′-H), 7.49 (t, J = 5.6 Hz, 2 H, 3′-, 5′-H), 7.20–7.18 (m, 2 H, 2′′-, 6′′-H), 7.12–7.09 (m, 2 H, 3′′-, 5′′-H), 3.96 (s, 3 H, CO_2Me), 3.30 (sept, J = 6.8 Hz, 1 H, *i*Pr), 1.46 (d, J = 6.8 Hz, 6 H, *i*Pr) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.55 (C_b), 164.65 (CO_2Me), 154.80 (7-C), 153.71 (4′′-C), 145.49 (a-C), 144.73 (3-C), 143.75 (3a-C), 143.32 (2-C), 141.58 (6-C), 140.20 (8-C), 136.24 (2′′- or 6′′-C), 136.19 (4-C), 134.74 (1′-C), 133.79 (2′′- or 6′′-C), 133.69 (1′′-C), 133.66 (4′-C), 130.89 (5-C), 129.73 (3′,5′-C), 129.50 (2′,6′-C), 125.79 (3′′- or 5′′-C), 125.42 (3′′- or 5′′-C), 124.08 (8a-C), 118.82 (1-C), 114.05 [$C(CN)_2$], 113.98 [$C(CN)_2$], 112.93 [$C(CN)_2$], 112.19 [$C(CN)_2$], 87.41 [$C(CN)_2$], 74.93 [$C(CN)_2$], 51.54 (CO_2Me), 39.31 (*i*Pr), 24.43 (*i*Pr) ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2962 (w), 2208 (s), 1699 (s), 1600 (m), 1521 (m), 1504 (s), 1442 (s), 1421 (s), 1400 (m), 1382 (s), 1303 (w), 1272 (w), 1128 (w), 1109 (w), 1085 (w), 1047 (w), 1026 (w), 1001 (w), 974 (w), 902 (w), 840 (w), 808 (w), 779 (w), 767 (w), 729 (w), 692 (w), 663 (w), 648 (w), 466 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 292 (4.34), 393 (4.26), 641 (4.43) nm. HRMS (ESI) calcd. for $C_{35}H_{24}N_4O_2$ + Na$^+$ [M + Na]$^+$ 555.1797; found 555.1791. $C_{35}H_{24}N_4O_2\cdot 1/10\,CHCl_3$ (532.19): calcd. C 77.42, H 4.46, N 10.29; found C 77.41, H 4.54, N 10.22.

{4-[3,3-Dicyano-1-[5-isopropyl-3-(methoxycarbonyl)azulen-1-yl]-2-thienylprop-2-en-1-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (6)



TCNQ (153 mg, 0.75 mmol) was added to a solution of **2** (167 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux for 3 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and preparative GPC with $CHCl_3$ to give **6** (250 mg, 93%); m.p. 160.0–166.0 °C (AcOEt). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.92 (s, 1 H, 8-H), 8.36 (d, J = 10.0 Hz, 1 H, 4-H), 8.18 (s, 1 H, 2-H), 7.71 (dd, J = 4.1, 1.1 Hz, 1 H, 3′-H), 8.02 (d, J = 10.0 Hz, 1 H, 6-H), 7.87 (dd, J = 5.2, 1.1 Hz, 1 H, 5′-H), 7.70 (dd, J = 10.0, 10.0 Hz, 1 H, 5-H), 7.81 (dd, J = 5.2, 4.1 Hz, 1 H, 4′-H), 7.23–7.19 (m, 2 H, 3′′-, 5′′-H), 7.14–7.09 (m, 2 H, 2′′-, 6′′-H), 3.96 (s, 3 H, CO_2Me), 3.32 (sept, J = 6.8 Hz, 1 H, *i*Pr), 1.47 (d, J = 6.8 Hz, 6 H, *i*Pr) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.70 (CO_2Me), 162.66 (b-C), 154.95 (7-C), 154.01 (4′′-C), 145.00 (a-C), 144.89 (3-C), 143.71 (3a-C), 142.83 (2-C), 141.71 (6-C), 140.29 (8-C), 138.16 (2′-C), 137.78 (5′-C), 136.64 (3′-C), 136.13 (4-C), 135.97 (3′′- or 5′′-C), 133.81 (3′′- or 5′′-C), 132.08 (1′′-C), 131.10 (5-C), 130.07 (4′-C), 125.72 (2′′- or 6′′-C), 125.29 (2′′- or 6′′-C), 123.37 (8a-C), 119.06 (1-C), 114.13 [$C(CN)_2$], 144.03 [$C(CN)_2$], 113.51 [$C(CN)_2$], 112.61 [$C(CN)_2$], 80.79 [$C(CN)_2$], 74.78 [$C(CN)_2$], 51.60 (CO_2Me), 39.39 (*i*Pr), 24.50 (*i*Pr) ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2960 (w), 2208 (s), 1699 (s), 1602 (m), 1521 (m), 1506 (s), 1444 (s), 1421 (s), 1407 (m), 1384 (s), 1361 (s), 1305 (w), 1276 (w), 1217 (s), 1193 (s), 1139 (w), 1128 (w), 1085 (w), 1062 (w), 1047 (w), 1020 (w), 999 (w), 972 (w), 929 (w), 877 (w), 840 (m), 812 (w), 779 (w), 729 (w), 669 (w), 657 (w), 565 (w), 466 (w), 416 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 304 (4.58), 314 sh (4.56), 364 (4.40), 626 (4.47) nm. HRMS (ESI) calcd. for $C_{33}H_{22}N_4O_2S$ + Na$^+$ [M + Na]$^+$ 561.1361; found 561.1356. $C_{33}H_{22}N_4O_2S$ (538.62): calcd. C 73.59, H 4.12, N 10.40; found C 77.41, H 4.41, N 10.35.

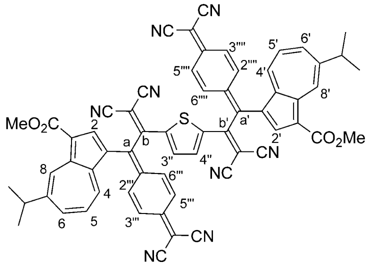
2,2′-(1,4-Phenylenebis{[1,1-dicyano-3-[5-isopropyl-3-(methoxycarbonyl)azulen-1-yl]prop-1-en-2-yl-3-ylidene]cyclohexa-2,5-diene-4,1-diylidene})dimalononitrile (7)



TCNQ (306 mg, 1.50 mmol) was added to a solution of **3** (289 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux for 6 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and Bio-Beads with CH_2Cl_2 to give **7** (464 mg, 94%); m.p. 225.0–229.0 °C (AcOEt). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.90 (s, 2 H, 8-H), 8.20 (d, J = 10.0 Hz, 2 H, 4-H), 8.10 (s, 2 H, 2-H), 8.03 (d, J = 10.0 Hz, 2 H, 6-H), 7.74 (s, 4 H, Ph), 7.68 (dd, J = 10.0, 10.0 Hz, 2 H, 5-

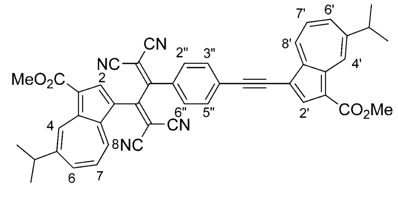
H), 7.23–7.18 (m, 4 H, 3′′′-, 5′′′-, 3′′′′-, 5′′′′-H), 7.04–7.02 (m, 4 H, 2′′′-, 6′′′-, 2′′′′-, 6′′′′-H), 3.96 (s, 6 H, CO$_2$Me), 3.32 (sept, *J* = 6.5 Hz, 2 H, *i*Pr), 1.46 (d, *J* = 6.5 Hz, 12 H, *i*Pr) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 169.82, 164.55 (CO$_2$Me), 155.26 (7-, 7′-C), 153.40 (4′′′-, 4′′′′-C), 144.74 (1-, 1′-C), 143.76 (3a-, 3a′-C), 143.42, 142.69 (2-, 2′-C), 141.96 (6-, 6′-C), 140.55 (8-, 8′-C), 138.45 (Ph-C), 136.14, (4-, 4′-C) 135.93 (3′′′-, 3′′′′- or 5′′′-, 5′′′′-C), 133.75 (3′′′-, 3′′′′- or 5′′′-, 5′′′′-C), 133.12 (1′′′-, 1′′′′-C), 131.10 (5-, 5′-C), 130.29 (Ph-C), 126.28 (2′′′-, 2′′′′- or 6′′′-, 6′′′′-C), 126.06 (2′′′-, 2′′′′- or 6′′′-, 6′′′′-C), 123.07 (8a-, 8a′-C), 119.14 (1-, 1′-C), 113.81 [C(CN)$_2$], 113.76 [C(CN)$_2$], 112.20 [C(CN)$_2$], 111.61 [C(CN)$_2$], 89.66 [C(CN)$_2$], 76.29 [C(CN)$_2$], 51.73 (CO$_2$Me), 39.41 (*i*Pr), 24.50 (*i*Pr) ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2962 (w), 2210 (s), 1699 (s), 1600 (m), 1521 (m), 1506 (s), 1442 (s), 1421 (s), 1400 (m), 1380 (s), 1355 (m), 1303 (w), 1278 (w), 1218 (s), 1193 (s), 1128 (w), 1107 (w), 1085 (w), 1047 (w), 1033 (w), 904 (w), 840 (w), 777 (w), 729 (w), 663 (w), 648 (w), 468 (w) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ (ε, L mol^{-1} cm^{-1}) = 238 (4.87), 292 (4.94), 362 (4.74), 627 (4.70) nm. HRMS (ESI) calcd. for $C_{64}H_{42}N_8O_4$ + Na$^+$ [M + Na]$^+$ 1009.3227; found 1009.3221. $C_{64}H_{42}N_8O_4\cdot 1/2\,H_2O$ (987.07): calcd. C 77.17, H 4.35, N 11.25; found C 77.19, H 4.47, N 11.19.

2,2′-(2,5-Thiophenediylbis{[1,1-dicyano-3-(5-isopropyl-3-(methoxycarbonyl)azulen-1-yl)prop-1-en-2-yl-3-ylidene]cyclohexa-2,5-diene-4,1-diylidene})dimalononitrile (8)



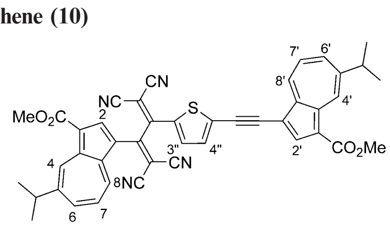
TCNQ (306 mg, 1.50 mmol) was added to a solution of **4** (292 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux for 12 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/ethyl acetate (1:1) and preparative GPC with CHCl$_3$ to give **8** (457 mg, 92%) as purple crystals; m.p. 230.0–234.0 °C (CHCl$_3$). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 9.91 (s, 2 H, 8-, 8′-H), 8.24 (d, *J* = 10.0 Hz, 2 H, 4-, 4′-H), 8.10 (s, 2 H, 2-, 2′-H), 8.05 (d, *J* = 10.0 Hz, 2 H, 6-, 6′-H), 7.93 (s, 2 H, 3′′-, 4′′-H), 7.69 (dd, *J* = 10.0, 10.0 Hz, 2 H, 5-, 5′-H), 7.21 (dd, *J* = 9.6, 1.6 Hz, 2 H, 3′′′-, 3′′′′-H), 7.17 (dd, *J* = 9.6, 1.6 Hz, 2 H, 5′′′-, 5′′′′-H), 7.01 (dd, *J* = 9.6, 1.6 Hz, 2 H, 2′′′-, 2′′′′-H), 6.98 (dd, *J* = 9.6, 1.6 Hz, 2 H, 6′′′-, 6′′′′-H), 3.98 (s, 6 H, CO$_2$Me), 3.33 (sept, *J* = 6.8 Hz, 2 H, *i*Pr), 1.47 (d, *J* = 6.8 Hz, 12 H, *i*Pr) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 164.54 (CO$_2$Me), 160.28 (b-, b′′-C), 155.48 (7-, 7′-C), 153.55 (4′′′-, 4′′′′-C), 145.18 (2′′-, 5′′-C), 145.02 (3-, 3′-C), 143.68 (3a-, 3a′-C), 142.30 (a-, a′-C), 142.19 (2-, 2′-C), 142.10 (6-, 6′-C), 140.54 (8-, 8′-C), 136.49, (4-, 4′-C) 135.68 (3′′-, 4′′-C), 135.58 (2′′′-, 2′′′′-C), 132.97 (6′′′-, 6′′′′-C), 132.58 (1′′′-, 1′′′′-C), 131.60 (5-, 5′-C), 126.20 (5′′′-, 5′′′′-C), 125.93 (3′′′-, 3′′′′-C), 122.25 (8a-, 8a′-C), 119.26 (1-, 1′-C), 113.81 [C(CN)$_2$], 113.77 [C(CN)$_2$], 112.58 [C(CN)$_2$], 111.71 [C(CN)$_2$], 85.37 [C(CN)$_2$], 76.11 [C(CN)$_2$], 51.78 (CO$_2$Me), 39.42 (*i*Pr), 24.50 (*i*Pr) ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2960 (w), 2208 (s), 1699 (s), 1600 (m), 1521 (m), 1506 (s), 1442 (s), 1419 (s), 1400 (s), 1382 (s), 1363 (s), 1303 (w), 1284 (m), 1217 (s), 1193 (s), 1128 (w), 1085 (w), 1045 (w), 1029 (w), 999 (w), 972 (w), 929 (w), 898 (m), 877 (w), 840 (m), 810 (w), 777 (w), 729 (w), 669 (w), 655 (w), 468 (w), 416 (w) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ (ε, L mol^{-1} cm^{-1}) = 240 (4.76), 294 (4.82), 314 sh (4.71), 391 (4.67), 590 (4.69) nm. HRMS (ESI) calcd. for $C_{62}H_{40}N_8O_4S$ + Na$^+$ [M + Na]$^+$ 1015.2791; found 1015.2785. $C_{62}H_{40}N_8O_4S\cdot 1/2\,CHCl_3$ (993.10): calcd. C 71.39, H 4.09, N 10.64; found C 71.30, H 3.88, N 10.64.

1-[2-[5-Isopropyl-3-(methoxycarbonyl)azulen-1-yl]-1,1,4,4-tetracyanobutadien-3-yl]-4-[[5-isopropyl-3-(methoxycarbonyl)azulen-1-yl]-ethynyl]benzene (9)



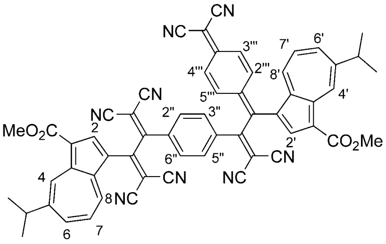
TCNE (320 mg, 2.50 mmol) was added to a solution of **3** (1.15 g, 2.00 mmol) in ethyl acetate (20 mL). The resulting mixture was heated at reflux for 2 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/ethyl acetate (1:1) and Bio-Beads with CH$_2$Cl$_2$ to give **9** (1.25 g, 88%) as purple crystals, and **13** (67 mg, 4%) as reddish purple crystals; m.p. 165.0–168.0 °C (decomp.). ^{1}H NMR (400 MHz, CDCl3): δ = 10.04 (dd, *J* = 2.0 Hz, 1 H, 4-H), 9.78 (dd, *J* = 2.0 Hz, 1 H, 4′-H), 8.66 (d, *J* = 10.0 Hz, 1 H, 8-H), 8.51 (s, 1 H, 2-H), 8.50 (d, *J* = 10.0 Hz, 1 H, 8′-H), 8.35 (s, 1 H, 2′-H), 8.17 (d, *J* = 10.0 Hz, 1 H, 6-H), 8.00 (dd, *J* = 10.0, 10.0 Hz, 1 H, 7-H), 7.90–7.88 (m, 3 H, 6′-H, 2′′-, 6′′-H), 7.77 (d, *J* = 8.8 Hz, 2 H, 3′′-, 5′′-H), 7.60 (dd, *J* = 10.0, 10.0 Hz, 1 H, 7′-H), 3.97 (s, 3 H, CO$_2$Me), 3.96 (s, 3 H, CO$_2$Me), 3.37 (sept, *J* = 6.8 Hz, 1 H, *i*Pr), 3.27 (sept, *J* = 6.8 Hz, 1 H, *i*Pr), 1.48 (d, *J* = 6.8 Hz, 6 H, *i*Pr), 1.44 (d, *J* = 6.8 Hz, 6 H, *i*Pr) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 167.90, 165.22, 164.3824, 160.69, 157.08, 151.68, 146.20, 145.38, 143.32, 142.56, 142.49, 141.99, 141.82, 140.80, 139.83, 138.77, 137.60, 136.21, 132.30, 132.27, 131.17, 130.46, 129.94, 128.25, 119.48, 115.74, 113.69, 112.48, 112.32, 111.51, 107.65, 93.43, 92.45, 86.19, 80.67, 51.70, 51.25, 39.48, 39.29, 24.57, 24.46 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2961 (m), 2220 (m), 2185 (s), 1697 (s), 1597 (m), 1552 (w), 1525 (m), 1494 (s), 1444 (s), 1418 (s), 1365 (m), 1319 (w), 1296 (w), 1272 (w), 1236 (m), 1213 (s), 1178 (m), 1134 (w), 1076 (w), 1033 (w), 1001 (w), 962 (w), 898 (w), 875 (w), 844 (w), 808 (w), 777 (w), 746 (w), 729 (w), 663 (w), 648 (w), 590 (w) cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ (ε, L mol^{-1} cm^{-1}) = 242 (4.75), 300 (4.80), 348 sh (4.51), 400 (4.47), 508 (4.45) nm. HRMS (ESI) calcd. for $C_{46}H_{34}N_4O_4$ + Na$^+$ [M + Na]$^+$ 729.2478; found 729.2472. $C_{46}H_{34}N_4O_4\cdot H_2O$ (706.79): calcd. C 76.23, H 5.01, N 7.73; found C 75.98, H 5.05, N 7.81.

2-[2-[5-Isopropyl-3-(methoxycarbonyl)azulen-1-yl]-1,1,4,4-tetracyanobutadien-3-yl]-5-[[5-isopropyl-3-(methoxycarbonyl)azulen-1-yl]-ethynyl]thiophene (10)



TCNE (320 mg, 2.50 mmol) was added to a solution of **4** (1.17 g, 2.00 mmol) in ethyl acetate (20 mL). The resulting mixture was heated at reflux for 2 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and Bio-Beads with CH_2Cl_2 to give **10** (1.25 g, 88%) as purple crystals, and **14** (84 mg, 5%) as reddish purple crystals; m.p. 226.0–228.0 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (dd, J = 2.0 Hz, 1 H, 4-H), 9.79 (s, 1 H, 4′-H), 8.62 (d, J = 10.0 Hz, 1 H, 8-H), 8.53 (d, J = 10.0 Hz, 1 H, 8′-H), 8.49 (s, 1 H, 2-H), 8.28 (s, 1 H, 2′-H), 8.18 (d, J = 10.0 Hz, 1 H, 6-H), 8.02 (dd, J = 10.0, 10.0 Hz, 1 H, 7-H), 7.96 (d, J = 4.0 Hz, 1 H, 3′′-H), 7.92 (d, J = 10.0 Hz, 1 H, 6′-H), 7.65 (dd, J = 10.0, 10.0 Hz, 1 H, 7′-H), 7.42 (d, J = 4.0 Hz, 1 H, 3′′-H), 3.97 (s, 3 H, CO_2Me), 3.96 (s, 3 H, CO_2Me), 3.36 (sept, J = 6.8 Hz, 1 H, *i*Pr), 3.27 (sept, J = 6.8 Hz, 1 H, *i*Pr), 1.48 (d, J = 6.8 Hz, 6 H, *i*Pr), 1.44 (d, J = 6.8 Hz, 6 H, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.07, 164.41, 159.92, 157.73, 157.07, 152.44, 146.34, 145.51, 143.41, 142.51, 142.43, 142.24, 142.00, 140.70, 140.25, 139.11, 138.23, 137.94, 137.89, 137.85, 136.44, 134.47, 132.75, 132.38, 128.87, 119.39, 118.76, 116.33, 113.59, 113.31, 112.48, 112.24, 106.66, 101.60, 101.59, 100.46, 87.039, 80.55, 78.16, 51.68, 51.34, 39.49, 39.35, 24.55, 24.47 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2960 (m), 2218 (m), 2171 (s), 1701 (s), 1488 (s), 1448 (s), 1415 (s), 1402 (s), 1365 (s), 1348 (s), 1274 (w), 1238 (m), 1213 (s), 1180 (m), 1134 (m), 1112 (m), 1064 (m), 1049 (m), 1031 (w), 964 (w), 918 (w), 898 (w), 873 (w), 840 (w), 806 (m), 775 (m), 732 (w), 686 (w), 659 (w), 648 (w), 590 (w), 559 (w), 540 (w), 505 (w), 461 (w), 441 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 240 (4.73), 298 (4.73), 382 sh (4.39), 410 (4.44), 550 (4.61) nm. HRMS (ESI) calcd. for $C_{44}H_{32}N_4O_4S$ + Na^+ [M + Na]$^+$ 735.2042; found 735.2036. $C_{44}H_{32}N_4O_4S$ (712.82): calcd. C 74.14, H 4.52, N 7.86; found C 73.77, H 4.76, N 7.97.

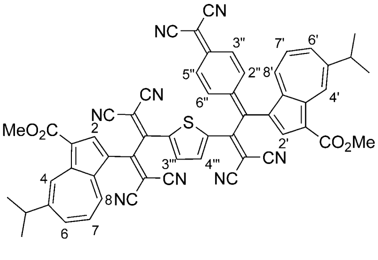
Compound 11



Reaction with 9 and TCNQ: TCNQ (153 mg, 0.75 mmol) was added to a solution of **9** (353 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux for 6 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and Bio-Beads with CH_2Cl_2 to give **11** (383 mg, 84%) as deep-green crystals.

Reaction with 3 and TCNE/TCNQ: TCNE (96 mg, 0.75 mmol) and TCNQ (153 mg, 0.75 mmol) were added to a solution of **3** (578 mg, 1.00 mmol) in ethyl acetate (20 mL). The resulting mixture was heated at reflux for 6 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and preparative GPC with $CHCl_3$ to give **11** (273 mg, 30%), **7** (286 mg, 29%), and **13** (267 mg, 32%); m.p. 214.0–217.0 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.04 (dd, J = 2.0 Hz, 1 H, 4-H), 9.92 (dd, J = 2.0 Hz, 1 H, 4′-H), 8.42 (d, J = 10.0 Hz, 1 H, 8-H), 8.24 (d, J = 10.0 Hz, 1 H, 8′-H), 8.22 (s, 1 H, 2-H), 8.21 (d, J = 10.0 Hz, 1 H, 6-H), 8.22 (s, 1 H, 2′-H), 8.02 (d, J = 10.0 Hz, 1 H, 6′-H), 8.02 (dd, J = 10.0, 10.0 Hz, 1 H, 7-H), 7.85 (m, 4 H, 2′′-, 3′′-, 5′′-, 6′′-H), 7.69 (dd, J = 10.0, 10.0 Hz, 1 H, 7′-H), 7.28–7.20 (m, 2 H, 3′′′-, 4′′′-H), 7.11–7.06 (m, 2 H, 5′′′-, 6′′′-H), 3.97 (s, 6 H, CO_2Me), 3.37 (sept, J = 6.8 Hz, 1 H, *i*Pr), 3.32 (sept, J = 6.8 Hz, 1 H, *i*Pr), 1.48 (d, J = 6.8 Hz, 6 H, *i*Pr), 1.46 (d, J = 6.8 Hz, 6 H, *i*Pr) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.70, 166.92, 164.48, 164.14, 158.96, 157.59, 155.14, 153.41, 146.29, 144.77, 143.74, 143.57, 142.95, 142.90, 142.08, 142.00, 141.95, 141.87, 140.98, 140.42, 139.17, 137.68, 136.11, 136.02, 135.73, 133.99, 133.31, 132.59, 131.12, 130.57, 130.48, 126.19, 125.95, 123.21, 119.84, 119.06, 118.77, 113.87, 113.81, 113.36, 112.35, 112.26, 111.62, 111.25, 110.50, 90.53, 89.92, 80.29, 75.73, 51.74, 51.56, 39.44, 39.27, 24.36 ppm. IR (KBr disk): $\tilde{\nu}_{max}$ = 2962 (m), 2210 (s), 1701 (s), 1602 (w), 1504 (s), 1442 (s), 1419 (s), 1400 (m), 1382 (m), 1365 (m), 1290 (w), 1217 (s), 1193 (s), 1136 (w), 1087 (w), 1047 (w), 1031 (w), 999 (w), 931 (w), 879 (w), 842 (w), 812 (w), 779 (w), 729 (w), 671 (w), 594 (w), 561 (w), 518 (w), 470 (w), 441 (w), 408 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 240 (4.96), 262 (4.91), 296 (4.96), 432 (4.90), 586 (4.64) nm. HRMS (ESI) calcd. for $C_{58}H_{38}N_8O_4$ + Na^+ [M + Na]$^+$ 933.2914; found 933.2909. $C_{58}H_{38}N_8O_4$ (910.97): calcd. C 76.23, H 5.01, N 7.73; found C 75.98, H 5.05, N 7.81.

Compound 12



Reaction with 10 and TCNQ: TCNQ (153 mg, 0.75 mmol) was added to a solution of **10** (354 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux for 6 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and by preparative GPC with $CHCl_3$ to give **12** (390 mg, 85%) as deep-green crystals.

Reaction with 4 and TCNE/TCNQ: TCNE (96 mg, 0.75 mmol) and TCNQ (153 mg, 0.75 mmol) were added to a solution of **4** (584 mg, 1.00 mmol) in ethyl acetate (20 mL). The resulting mixture was heated at reflux for 6 h under Ar. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (1:1) and by preparative GPC with $CHCl_3$ to give **12** (275 mg, 30%), **8** (268 mg, 27%), and **14** (285 mg, 34%); m.p. 210.0–213.0 °C (AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (dd, J = 2.0 Hz, 1 H, 4-H), 9.94 (dd, J = 2.0 Hz, 1 H, 4′-H), 8.40 (d, J = 10.0 Hz, 1 H, 8-H), 8.28 (d, J = 10.0 Hz, 1 H, 8′-H), 8.22 (d, J = 10.0 Hz, 1 H, 6-H), 8.18 (s, 1 H, 2-H), 8.13 (d, J = 4.0 Hz, 1 H, 3′′′-H), 8.06–8.00 (m, 3 H, 7, 2′-, 6′-H), 7.93 (d, J = 4.0 Hz, 1 H, 4′′′-H), 7.71 (dd, J = 10.0, 10.0 Hz, 1 H, 7′-H), 7.28 (dd, J = 7.6, 2.0 Hz, 1 H, 3′′-H), 7.20 (dd, J = 7.6, 2.0 Hz, 1 H, 5′′-H), 7.06 (d, 2 H, 2′′-, 6′′-H), 3.98 (s, 3 H, CO_2Me), 3.97 (s, 3 H, CO_2Me), 3.38 (sept, J = 6.8 Hz, 1 H, *i*Pr), 3.33 (sept, J = 6.8 Hz, 1 H, *i*Pr), 1.49 (d, J = 6.8 Hz, 6 H, *i*Pr), 1.47 (d, J = 6.8 Hz, 6 H, *i*Pr) ppm. Low solubility prevented ^{13}C NMR spectroscopy. IR (KBr disk): $\tilde{\nu}_{max}$ = 2962 (m), 2210 (s), 1701 (s), 1602 (w), 1523 (m), 1504 (s), 1442 (s), 1419 (s), 1400 (m), 1382 (m), 1363 (m), 1290 (w), 1217 (s), 1193 (s), 1136 (w), 1087 (w), 1047 (w), 1029 (w), 1001 (w), 900 (w), 842 (w), 810 (w), 779 (w), 729 (w), 671 (w), 447 (w), 408 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 240 (4.78), 262 sh (4.73), 296 (4.78), 432 (4.73), 586 (4.46) nm. HRMS (ESI) calcd. for $C_{56}H_{36}N_8O_4S$ + Na^+

939.2478; found 939.2472. $C_{56}H_{36}N_8O_4S$ (917.00): calcd. C 76.23, H 5.01, N 7.73; found C 75.98, H 5.05, N 7.81.

Supporting Information (see also the footnote on the first page of this article): UV/Vis spectra and cyclic voltammograms of reported compounds.

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[1] a) J. Ferraris, D. O. Cowan, V. Walatka Jr., J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948–949; b) E. B. Vickers, T. D. Selby, M. S. Thorum, M. L. Taliaferro, J. S. Miller, *Inorg. Chem.* **2004**, *43*, 6414–6420; c) E. B. Vickers, I. D. Giles, J. S. Miller, *Chem. Mater.* **2005**, *17*, 1667–1672.

[2] a) M. Kivala, C. Boudon, J. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4731–4733; b) P. Reutenauer, M. Kivala, P. D. Jarowski, C. Boudon, J. P. Gisselbrecht, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4898–4900; c) M. Kivala, C. Boudon, J. Gisselbrecht, B. Enko, P. Seiler, I.-B. Müller, N. Langer, P.-D. Jarowski, G. Gescheidt, F. Diederich, *Chem. Eur. J.* **2009**, *15*, 4111–4123.

[3] a) D. S. Acker, W. R. Hertler, *J. Am. Chem. Soc.* **1962**, *84*, 3370–3374; b) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, W. E. Mochel, *J. Am. Chem. Soc.* **1962**, *84*, 3374–3387; c) W. R. Hertler, H. D. Hartzler, D. S. Acker, R. E. Benson, *J. Am. Chem. Soc.* **1962**, *84*, 3387–3393; d) J. K. Williams, *J. Am. Chem. Soc.* **1962**, *84*, 3478–3479; e) J. Ferraris, D. O. Cowan, V. Walatka Jr., J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948–949; f) N. Martin, J. L. Segura, C. Seoane, *J. Mater. Chem.* **1997**, *7*, 1661–1676; g) E. B. Vickers, T. D. Selby, M. S. Thorum, M. L. Taliaferro, J. S. Miller, *Inorg. Chem.* **2004**, *43*, 6414–6420; h) E. B. Vickers, I. D. Giles, J. S. Miller, *Chem. Mater.* **2005**, *17*, 1667–1672; i) K. Walzer, B. Maennig, M. Pfeiffer, K. Leo, *Chem. Rev.* **2007**, *107*, 1233–1271.

[4] K.-P. Zeller, Azulene. In *Houben-Weyl*, *Methoden der Organischen Chemie*, 4th ed. (Ed.: H. Kropf), Georg Thieme, Stuttgart, Germany, **1985**, vol. V, part 2c, pp. 127–418.

[5] T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Chem. Eur. J.* **2008**, *14*, 8398–8408.

[6] M. Kivala, C. Boudon, J. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Angew. Chem.* **2007**, *119*, 6473–6477; *Angew. Chem. Int. Ed.* **2007**, *46*, 6357–6360.

[7] Reactions between electron-rich acetylene derivatives and TCNE have recently been reported; a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, 737–739; b) T. Michinobu, C. Boudon, J. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905; c) M. Kivala, T. Stanoeva, T. Michinobu, B. Frank, G. Gescheidt, F. Diederich, *Chem. Eur. J.* **2008**, *14*, 7638–7647; d) J.-L. Alonso-Gómez, P. Schanen, P. Rivera-Fuentes, P. Seiler, F. Diederich, *Chem. Eur. J.* **2008**, *14*, 10564–10568; e) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248.

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