Azulene-based Donor-Acceptor Systems: Synthesis, Optical, and Electrochemical Properties

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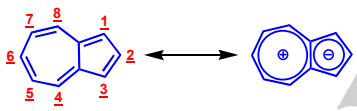
Dedicated to Professor Klaus Hafner on the occasion of his 90th birthday.

Abstract: Herein, we describe the synthesis and properties of azulene-substituted 1,1,4,4-tetracyanobutadienes (AzTCBDs) and heteroazulenyl TCBDs. TCBD derivatives were prepared in good to excellent yields *via* reaction of the corresponding 1-ethynylazulenes with tetracyanoethylene (TCNE). In contrast, the reaction between propargyl alcohols and the 1-azulenyl group in TCNE generated 2-aminofuran derivatives, which were transformed into 6-aminofulvenes with a 1-azulenyl substituent upon treatment with several amines. The optical and electrochemical properties of the AzTCBDs were clarified by UV/Vis and voltammetry. The AzTCBD derivatives exhibited electrochromism, showing a multi-step color change under electrochemical redox conditions. The multistage redox properties of AzTCBDs could be useful for the development of novel organic electronic materials.

1. Introduction

Since the discovery of efficient methods for the synthesis of azulene and its derivatives by Ziegler-Hafner[1] and Nozoe *et al*.[2] in the 1950's, many researchers have been fascinated by these compounds due to their singular reactivity and properties derived from their polarization structure, as well as their beautiful blue color.[3] Both the cationic and anionic structures of azulene are stabilized by resonance within the tropylium and cyclopentadienide substructures (Scheme 1). Azulene exerts a strongly electron-donating effect on substituents at the 1- and 3-positions (five-membered ring), whereas it exerts a strongly electron-withdrawing effect on substituents at the 4-, 6-, and 8-positions (seven-membered ring).



Scheme 1. Resonance structure and numbering scheme of azulene.

Recently, a variety of efficient and uncomplicated synthetic procedures for azulene derivatives have been prompted[4] owing to their useful applications in organic electronics,[5] medicinal chemistry,[6] bioimaging,[7] and stimuli-responsive materials.[8] We have also reported the preparation, reactivity, and properties (e.g., optical, electrochemical, and thermodynamic) of novel azulene derivatives with various π-electron systems.[9,10,11] The results revealed that azulene derivatives can be applied to functional materials based on their optical and electrochemical properties derived from their anomalous polarized structures.

Electrochromic molecules are generic names of compounds whose electronic spectra change with changes in potential or current, and are expected to be useful for applications in display materials, optical memory, and electrochemical switches.[12] In order to construct reversible electrochromic molecules, it is necessary to design multistage, reversible redox systems. To develop electrochromic molecules in which information input by potential or current is output as a drastic color change, we have investigated the synthesis as well as optical and electrochemical properties of azulene-substituted 1,1,4,4-tetracyanobutadienes (AzTCBD) derivatives and related compounds. Through these studies, we found that AzTCBDs displayed an intense intramolecular charge-transfer (ICT), as well as multistage reduction behavior. Moreover, we observed significant color changes of AzTCBDs under electrochemical reduction conditions.

Herein, we describe the broad applicability and efficiency of AzTCBD chromophores as terminal groups for the preparation of multistage redox systems and stabilized electrochromic materials.

2. Synthesis of TCBD Derivatives

Many reports on the synthesis of donor-acceptor systems based on TCBD derivatives have aimed towards the elucidation of their ICT characteristics and development of their applications in the material sciences. In 1981, Bruce *et al*. reported for the first time that TCBD derivatives were obtained in the reaction of ruthenium acetylide with tetracyanoethylene (TCNE).[13] First synthesis of TCBD derivatives consisting of pure organic compounds was established by Jen and his co-workers in 1999.[14] Yamashita and co-workers reported that alkyne derivatives with a 1,3-dithiol-2-ylidene moiety reacted with TCNE to give TCBD derivatives that showed amphoteric redox behavior in cyclic voltammetry (CV).[15] Trolez *et al*. demonstrated the reaction of ynamide derivatives with TCNE affording nitrogen-substituted TCBDs in good to excellent yields.[16] Michinobu *et al*. demonstrated that polymers embedded with TCBD units showed an ICT absorption band with a low energy band gap.[17] They also investigated their applications as ion sensors using polymer effects, digital memory,[18] and photovoltaic devices.[19] Diederich and co-workers primarily developed TCBD chemistry. Various donor-substituted TCBDs have been synthesized *via* the formal [2 + 2] CA–RE (cycloaddition-retroelectrocyclization) reaction between electron-rich alkynes and TCNE.[20] Moreover, new chromophores based on TCBD derivatives exhibit ICT with an intense absorption band in the visible region and can be applied in organic and optoelectronic materials.[21] Although these studies contributed greatly to the development of TCBD chemistry, the development of TCBD derivatives into electrochromic molecules by utilizing their multistage redox behavior is lacking.

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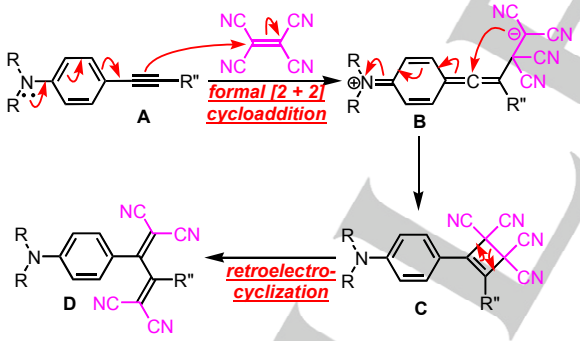
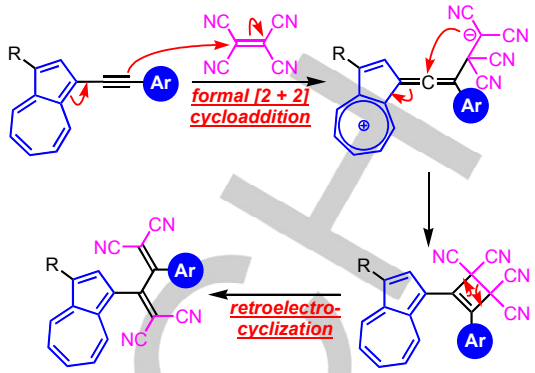
As described above, electron-rich alkynes react with electron-deficient alkenes [e.g., TCNE,[13−21] 7,7,8,8-tetracyanoquinodimethane (TCNQ),[22] dichlorodicyanoquinone (DDQ),[23] and dicyanoethene derivatives[24] among others[25] in a formal [2 + 2] cycloaddition (CA) to form a cyclobutene ring, which is followed by a retroelectrocyclization (RE) to give donor-acceptor type molecules. In the [2 + 2] CA−RE reaction, aromatic amines on terminal alkynes are excellent accelerating groups. For example, the reaction of an alkyne containing a dialkylanilino (DAA) substituent with TCNE instantaneously proceeds at room temperature to give TCBD derivatives quantitatively in most cases.[20a] A proposed mechanism for the [2 + 2] CA−RE reaction is illustrated in Scheme 2. Namely, nucleophilic addition of electron-rich alkyne **A** forms transient zwitterion **B**, which readily cyclizes to cyclobutene intermediate **C**. Strained intermediate **C** is transformed *via* an RE reaction to afford TCBD **D**. The detailed reaction mechanism of the [2 + 2] CA−RE reaction was investigated by Diederich *et al*. *via* kinetics and computational experiments.[26] The study revealed that the RE process of the cyclobutene intermediate was the rate-determining step of the reaction.

Similar to the reaction with TCNE, DAA-substituted alkynes react with TCNQ at room temperature to afford 7,7,8,8-dicyanoquinodimethanes (DCNQs) in quantitative yields in most cases.[21a] The addition of TCNQ usually occurs regioselectively to give one regioisomer, but alkynes possessing different donor groups could afford several regioisomers.[27] Acetylides[13, 28] and alkyne derivatives substituted with ferrocene,[29] tetrathiafulvalene,[30] and porphyrins[31] also undergo the [2 + 2] CA−RE reaction with TCNE and TCNQ to give the corresponding TCBDs and DCNQs in good to excellent yields.



Scheme 2. Plausible reaction mechanism for the [2 + 2] CA−RE reaction of DAA-substituted alkynes with TCNE.

Similar to the DAA substituent, the 1-position of the azulene ring is electron-donating, so the [2 + 2] CA-RE reaction of 1-ethynylazulenes is expected to proceed with TCNE and TCNQ. Actually, 1-ethynylazulene derivatives undergo the [2 + 2] CA−RE reaction with TCNE and TCNQ to generate 1-azulenyl TCBDs (1-AzTCBDs) and DCNQs (1-AzDCNQs) (Scheme 3). Utilizing highly reactive 1-ethynylazulenes, we prepared various AzTCBD derivatives on a variety of π-electron systems as described below.



Scheme 3. Plausible reaction mechanism of the [2 + 2] CA−RE reaction of 1-ethynylazulenes with TCNE.

3. 1-Azulenyl TCBDs with Aryl Substituents

In 2008, we reported the first reaction of 1-ethynylazulenes possessing two types of aryl terminal groups (i.e., phenyl or thienyl groups) with TCNE to afford 1-AzTCBDs **1**−**5** in good to excellent yields (86−97%) under mild conditions, i.e., room temperature or in refluxing ethyl acetate (Figure 1).[32] We also described the [2 + 2] CA−RE reaction of 1-ethynylazulenes with TCNQ to give the corresponding 1-AzDCNQs.[33] The formation of 1-AzTCBDs and 1-AzDCNQs indicates that the reactivity of the alkyne moiety in the [2 + 2] CA−RE reaction is significantly enhanced by the 1-azulenyl group, due to its strong electron-donating abilities.

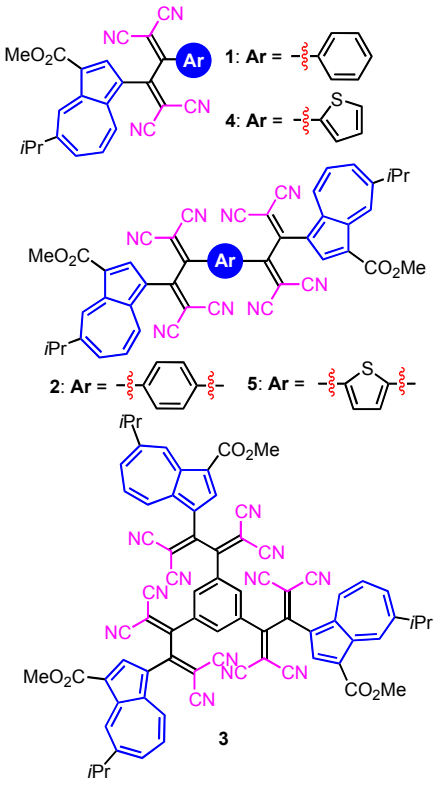
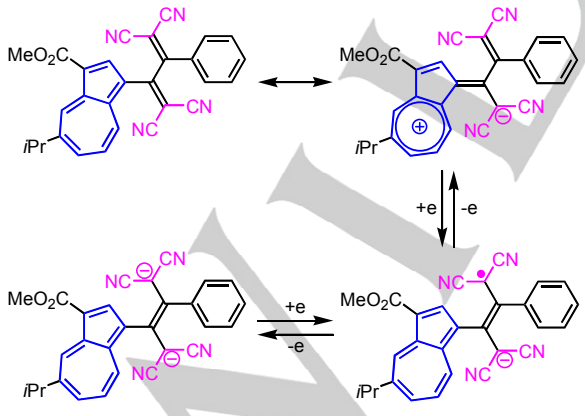


Figure 1. Structures of 1-AzTCBDs **1**–**5** with benzene and thiophene cores.

Analysis of 1-AzTCBDs **1**–**5** by ultraviolet-visible absorption (UV/Vis) spectrophotometry was carried out, in order to investigate the optical properties of these compounds. UV/Vis of 1-AzTCBDs **1**–**5** revealed a strong absorption band in the visible region caused by an ICT between the 1-azulenyl group and TCBD moieties, as illustrated by the resonance structure shown in Scheme 4.[32] Notably, 1-AzTCBDs **1**–**3** containing a benzene ring exhibited bathochromic shifts and increased extinction coefficients in their UV/Vis spectra with increasing numbers of 1-AzTCBD units substituted on the benzene ring (Table 1), suggesting the presence of an electronic interaction among the 1-AzTCBD units through the benzene moiety.

The redox potential of a compound can be a useful guide for the molecular design of organic electronic materials. Therefore, we investigated the redox behavior and potential of 1-AzTCBDs **1**–**5** using CV. The electrochemical reduction of 1-AzTCBDs **1**–**5** showed multi-step reduction waves in CV depending on the number of TCBD units in the molecule, even though compounds **2**, **3**, and **5** contain C_2 and C_3 symmetric structures. The redox behavior of the TCBD derivatives could be explained by the electron-transfer, as illustrated by 1-AzTCBD **1** in Scheme 4. Moreover, their first reduction potentials (E_1^{red}) also revealed a shift towards lower potentials depending on the number of 1-AzTCBDs in the molecule owing to the electronic communication between the TCBD units *via* the aromatic ring. Therefore, the use of π-electron systems with multiple 1-AzTCBD units is attractive for the molecular design of multistage redox systems.

Electrochromism is a phenomenon in which electronic spectra are reversibly changed upon electrochemical reactions.[12] 1-AzTCBDs exhibit such electrochromic behaviors. Multi-stage color changes were observed in the electrochemical reduction of bis-1-AzTCBD **5** with a thiophene core due to the hybrid structure of the violene-cyanine-violene moiety.[34]



Scheme 4. Resonance structure and redox behavior of 1-AzTCBD **1**.

Table 1. Absorption maxima [nm] in the visible region, coefficients (log ε) in dichloromethane, and first reduction potential[a] of **1**–**5**.

Compound	λ_{max} (log ε)[b]	E_1^{red} [V]
1	462 (4.04), 534 sh (3.88)	−0.61
2	444 (4.44), 540 sh (4.10)	−0.46
3	414 (4.60), 550 (4.38)	−0.40
4	460 (4.18)	−0.64
5	416 sh (4.64), 434 (4.67)	−0.31

[a] Measured by CV; V versus Ag/$AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1} and internal reference (Fc/Fc^+ = +0.15 V); Half-wave potentials $E^{red} = (E_{pc} + E_{pa})/2$ on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] sh = shoulder peak.

Changing the *p*-substituent on the benzene ring in 1-AzTCBD moiety allows the redox potential to be tuned and may lead to the construction of electrochromic molecules with higher stability. Thus, to clarify the effect of substituents on the optical and electrochemical properties of these compounds, we investigated the introduction of various functional groups onto the benzene ring, forming mono-, bis-, and tris-1-AzTCBDs **6**–**10** (Figure 2).[27,35] The optical and electrochemical properties of 1-AzTCBDs **6**–**10** depended on the nature of the substituent in the *p*-position on the benzene ring as well as the number of 1-AzTCBD units in the molecule. This phenomenon indicated the existence of electronic communication between the substituent on the benzene ring and TCBD unit *via* the connected π-system.

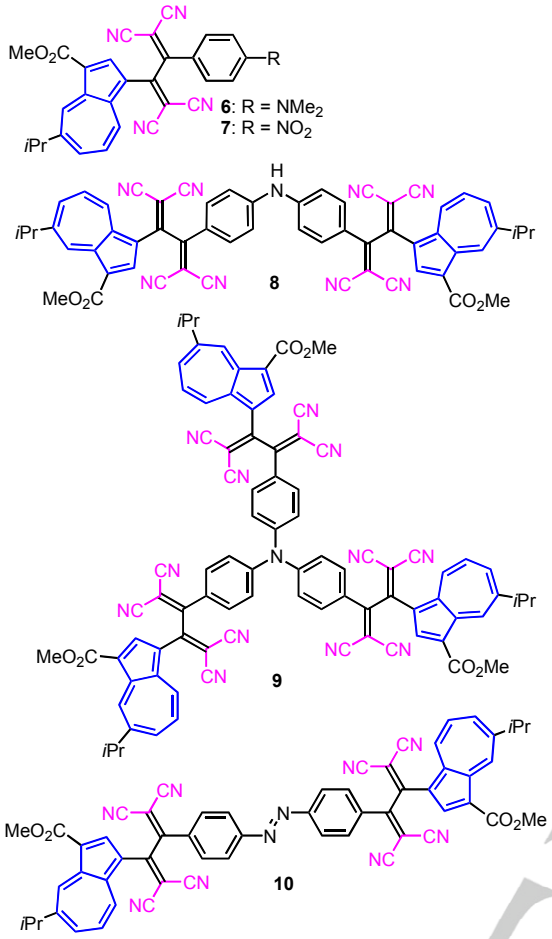
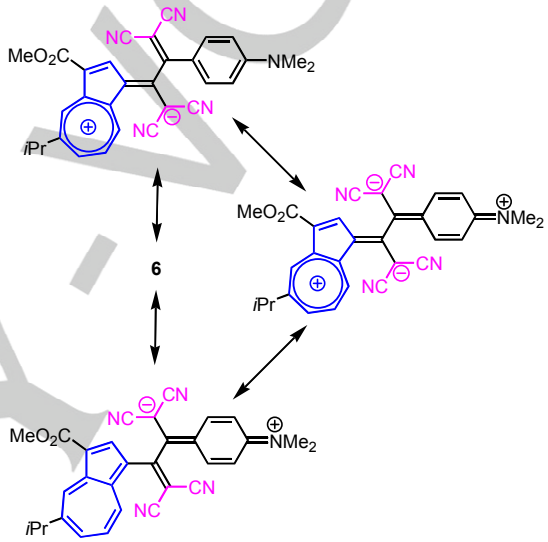


Figure 2. Structures of mono-, bis-, and tris-1-AzTCBDs **6**–**10** with aromatic cores.

1-AzTCBDs **6** (λ_{max} = 474 nm, log ε = 4.49), **8** (λ_{max} = 489 nm, log ε = 4.81), and **9** (λ_{max} = 503 nm, log ε = 4.86) exhibited broad absorption bands in the visible region; a bathochromic shift was observed with increasing numbers of substituted 1-AzTCBD units due to the π-extension through the connected arylamine moieties (Table 2). The bathochromic shift in the longest wavelength absorption band of 1-AzTCBD having a nitrobenzene unit **7** [λ_{max} = 533 (sh) nm, log ε = 3.86] and azobenzene substituent **10** [λ_{max} = 532 (sh) nm, log ε = 4.26] might be attributed to their decreased LUMO levels on account of the electron-withdrawing groups. 1-AzTCBD **6** exhibited a larger extinction coefficient than **1** and **7**, suggesting an ICT among the TCBD, amino, and azulenyl groups *via* resonance, as illustrated in Scheme 5. Hypsochromic solvatochromism of 1-AzTCBDs **6**–**10** was also revealed by changing the solvent from CH_2Cl_2 to *n*-hexane/CH_2Cl_2 mixtures. The solvatochromism indicates that 1-AzTCBDs **6**–**10** have a higher polarity in the excited state than in the ground state.[36]

Electrochemical reduction of 1-AzTCBDs **6**, **8**, and **9** resulted in two- or three-step waves in CV. The E_1^{red} of 1-AzTCBDs **6** (−0.78 V), **8** (−0.63 V), and **9** (−0.58 V) containing arylamines decreased with increasing numbers of TCBD units in the molecule (Table 2), indicating that multiple TCBD units lower the LUMO level and that the electron-accepting ability increases due to the π-conjugation with the arylamine cores. The E_1^{red} values of 1-AzTCBD **7** (−0.46 V) and **10** (−0.54 V) were less negative than those of **1**, **6**, **8**, and **9**, indicating that the electron-withdrawing group in the para-position on the benzene ring (i.e., nitro and azo substituents) directly reduced the LUMO level, as predicted from UV/Vis. Spectral changes of 1-AzTCBDs **6**–**10** were observed under constant-current reduction conditions.[37] For example, a new absorption appeared at around 750 nm for **8** upon electrochemical reduction, while the original absorption band gradually diminished.



Scheme 5. Resonance structure of 1-AzTCBD **6**.

Table 2. Absorption maxima [nm] in the visible region, coefficients (log ε) in dichloromethane, and first reduction potential[a] of **6**–**10**.

Compound	λ_{max} (log ε)[b]	E_1^{red} [V]
6	474 (4.49)	–0.78
7	421 (4.08), 533 sh (3.86)	–0.46
8	489 (4.81)	–0.63
9	503 (4.86)	–0.58
10	532 sh (4.26)	–0.54

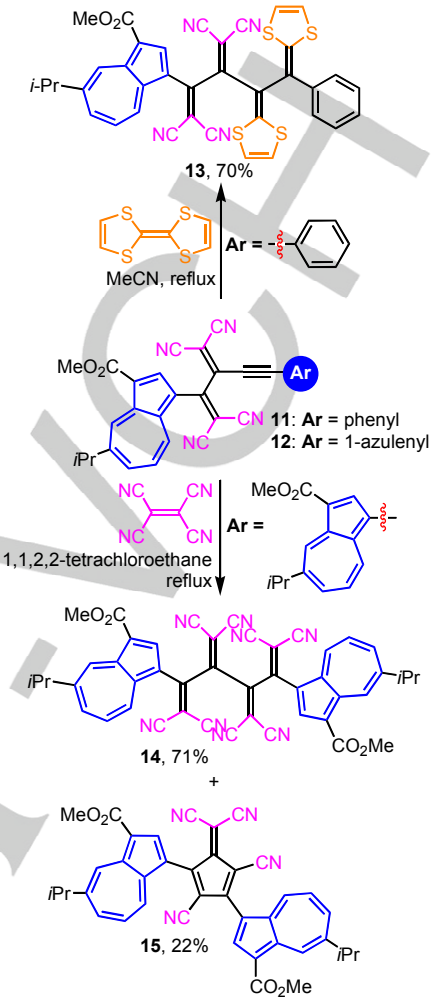
[a] Measured by CV; V versus Ag/$AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1} and internal reference (Fc/Fc^+ = +0.15 V); Half-wave potentials $E^{red} = (E_{pc} + E_{pa})/2$ on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] sh = shoulder peak.

As described above, even though the bis- and tris-1-AzTCBD derivatives have symmetrical structures, the CV of these compounds showed a multistage reduction wave due to the electrochemical interaction between the TCBD units *via* the central π-electron system. To construct multistage redox systems, we investigated the synthesis of 1-AzTCBDs bearing a 1,3,5-tri(1-azulenyl)benzene core, and studied their optical properties and redox behaviors. Unfortunately, these studies revealed that the expansion of the conjugated system *via* the 1,3,5-tri(1-azulenyl)benzene core was not effective and the electronic communication between the 1-AzTCBD units in the molecule was quite small.[38]

4. Sequential [2 + 2] CA−RE Reaction of 1-Azulenylbutadiynes with TCNE and TTF

In 1991, Hopf *et al*. reported the formal [2 + 2] CA−RE reaction of tetrathiafulvalene (TTF) with electron-deficient alkynes with dicyanoethylene substituents in the formation of 1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives with donor-acceptor structures.[39] Recently, Diederich *et al*. reported the preparation of dendralene-type chromophores with both TCBD and 1,2-bis(1,3-dithiol-2-ylidene)ethane units by the sequential [2 + 2] CA−RE reaction of TCNE and TTF with DAA-substituted butadiynes.[40] Inspired by this research, we examined the reaction of butadiyne derivatives possessing terminal 1-azulenyl groups. As a result, TCBD-TTF adduct **13** and dendralene **14** were prepared, and their multistage redox properties and extremely low reduction potentials were revealed.[41]

Similar to the reaction of 1-ethynylazulenes, 1-azulenylbutadiynes prepared from 1-ethynylazulene derivatives *via* Glaser-Hay coupling reacted with TCNE under mild conditions to give the corresponding 1-AzTCBDs **11** and **12** with aryl alkyne substituents. The alkyne moiety of **11** reacted with TTF to give TCBD-TTF adduct **13** (Scheme 6). In this case, the C≡C triple bond of **11** behaved as an electron-deficient alkyne due to the attached highly electron-withdrawing group, i.e., the TCBD moiety. On the other hand, the [2 + 2] CA−RE reaction of **12** with TCNE afforded dendralene **14**, along with 6,6-dicyanofulvene derivative **15** as a by-product. Since 6,6-dicyanofulvene **15** was obtained neither from **12** nor **14** upon reflux in 1,1,2,2-tetrachloroethane, TCNE may contribute to the generation of **15**. The 6,6-dicyanofulvene moiety can be used for further molecular transformations, because the derivative acts as an electron-deficient alkene and the [2 + 2] CA−RE reaction proceeds with electron-rich alkynes.[42]



Scheme 6. Synthesis of TCBD-TTF adduct **13**, dendralene **14**, and 6,6-dicyanofulvene **15**.

In regard to the electrochemical analysis, TCBD-TTF adduct **13** showed a one-stage oxidation wave (+0.57 V) in CV owing to the electrochemical oxidation of the 1,2-bis(1,3-dithiol-2-ylidene)ethane moiety. The E_1^{red} of **11** (−0.39 V) was much more positive than that of **13** (−0.80 V), indicating that the 1,2-bis(1,3-dithiol-2-ylidene)ethane unit on **13** leads to an increased LUMO level as compared to that of **11**. The E_1^{red} of **14** (+0.23 V) was not negative, indicating an increased electron-accepting ability due to the reduction of the LUMO level. Compound **15** also showed two-step reduction waves (−0.32 V and −0.59 V), due to the step-wise electrochemical reduction of the 6,6-dicyanofulvene moiety.

5. 1-Azulenyl TCBDs with 1-, 2-, and 6-Azulenyl Substituents

We have reported the preparation of novel π-electron molecules with various 2-azulenyl[10] or 6-azulenyl substituents[11] for the construction of multistage redox systems by utilizing the

unique electronic properties of azulenyl substituents. Since the anionic species are stabilized by 2-azulenyl and 6-azulenyl groups by resonance, TCBD and DCNQ derivatives with 1-azulenyl and 2- or 6-azulenyl groups should stabilize the redox cycle and lead to improved electrochromic properties. Therefore, we investigated the synthesis, physical properties, and electrochromic behaviors of TCBD derivatives with two azulenyl moieties (i.e., 1-azulenyl group and 1-, 2-, 6-azulenyl group).[43]

As mentioned in the previous section, the 1-azulenyl group has high electron donating properties and activates the [2 + 2] CA-RE reaction between the directly connected alkynes and TCNE. Therefore, 1-ethynylazulene reacts with TCNE to give the corresponding 1-AzTCBDs **16** (94% yield), despite the electron-withdrawing substituent on the azulene ring (i.e., methoxycarbonyl group). On the other hand, 2- and 6-ethynylazulenes without the 1-ethynylazulene moiety did not react with TCNE. These results indicate that 2- or 6-ethynylazulenes do not promote the reaction, likely because their insufficient electron-donating abilities are unfavorable for the [2 + 2] CA−RE reaction. Whereas, the [2 + 2] CA−RE reaction of 1-ethynylazulene derivatives with 1-, 2-, or 6-azulenyl groups with TCNE afforded TCBDs **17**−**22** with two azulenyl substituents in excellent yields (89−97% yields; Figure 3). Therefore, a highly electron-donating 1-azulenyl substituent on at least one alkyne terminal is indispensable for the [2 + 2] CA−RE of alkyne derivatives bearing 2- and 6-azulenyl groups.

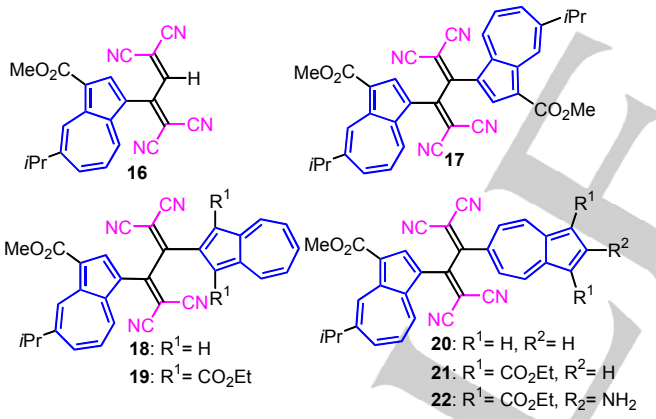
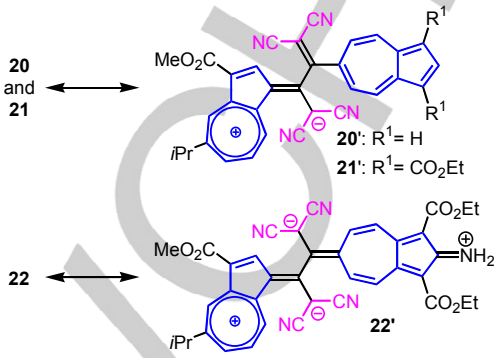


Figure 3. Structures of 1-AzTCBD **16** and TCBDs **17**−**22** with two azulenyl groups,

UV/Vis revealed that the absorption maxima of AzTCBDs **17**−**22** depended on the azulene substituent on the 1-AzTCBD moiety (Table 3). For example, **22** (λ_{max} = 510 nm) exhibits a comparatively strong absorption band in the visible region, although small absorption coefficients were observed for the longest wavelength absorption maxima of **20** [λ_{max} = 545 (sh) nm] and **21** [λ_{max} = 558 (sh) nm]. These differences are derived from the nature of the substituent at the 2-position of the azulene ring. In the case of AzTCBDs **20** and **21**, ICT arises only from the transition between the 1-azulenyl group and TCBD (Scheme 7, top). On the other hand, AzTCBD **22** shows a larger molar extinction coefficient due to the overlap of the transitions between TCBD and the 1-azulenyl and 2-amino-6-azulenyl group forming the quinoid structure by resonance (Scheme 7, bottom), similar to 1-AzTCBD **6**. [44]



Scheme 7. Resonance structures of 1-AzTCBD **20**, **21**, and **22**.

Two-step reduction waves appeared in the cyclic voltammograms of AzTCBDs **17**−**22** owing to the stepwise electrochemical reduction of the TCBD moiety (Table 3). The E_1^{red} of **19** was more positive than that of **18** owing to the substitution of two electron-withdrawing ethoxycarbonyl groups at the 1,3-positions. The E_1^{red} of **20** was more positive than that of **18**, revealing the higher electron-accepting ability of the 6-azulenyl group compared to that of the 2-azulenyl group. Although the ethoxycarbonyl groups were in the 1,3-positions of the azulene ring, TCBD **22** displayed the most negative E_1^{red} value among bis-AzTCBDs **20**−**22** with 6-azulenyl groups, since the 2-amino moiety of **22** increased the LUMO level owing to its electron-donating nature. Spectroelectrochemical measurements revealed that TCBDs **17**−**22** exhibited spectral changes under electrochemical reduction conditions. Specifically, the electrochemical reduction of a purple-colored solution of **17** resulted in an orange-colored solution, and a new absorption band appeared at 700 nm. This phenomenon was ascribed to the violene-violene structure of **17**.[34] Under electrochemical reduction conditions, an absorption band of **21** steadily developed in the near-infrared region, and the subsequent reverse oxidation of the reduced species resulted in the reappearance of the original spectrum of **21**. Overall, TCBDs **18**−**22** bearing both 1-azulenyl and 2- or 6-azulenyl groups show reversible and remarkable color changes under redox conditions as compared to the TCBDs having only 1-azulenyl group described in the previous sections. These results suggest that the 2- or 6-azulenyl group stabilizes radical ions and/or the ionic state generated by the electrochemical redox reaction.

As part of the development of the above-mentioned research, we demonstrated the synthesis and properties of TCBD derivatives **23**−**28** with three azulenyl substituents (Figure 4).[45] The extinction coefficients of **23**−**28** increased with increasing numbers of TCBD units, as compared to those of TCBDs **17**−**22**. These effects intimate an overlap of ICT arising from the

resonance between the central 1,3-azulendiyl core and two AzTCBD units.

Even though TCBDs **23**–**28** have a symmetric structure with respect to the central 1,3-azulendiyl core, these compounds showed four-step reduction waves in their cyclic voltammograms, owing to the electrochemical interaction between the two TCBD units *via* the cross-conjugation through the central 1,3-azulendiyl core. Furthermore, TCBDs **23**–**28** exhibited lower first reduction potentials than TCBDs **17**–**22**, because of the stronger electron-accepting nature of **23**–**28** derived from the TCBD units. Under electrochemical reduction conditions, a solution of TCBD **27** changed from red to blue, and the absorption band in the near-infrared region gradually increased. When the reduced species of **27** was oxidized in the electrochemical reaction, the parent spectrum was regenerated, as was the original red color. This reversible color change suggests that the anionic species generated by electrochemical reduction are extremely stable.

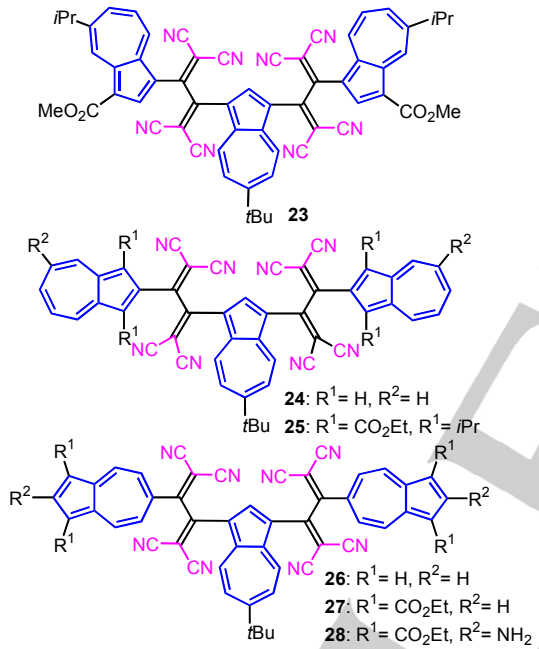


Figure 4. Structures of TCBDs **23**–**28** with two azulenyl substituents.

Table 3. Absorption maxima [nm] in the visible region, coefficients (log ε) in dichloromethane, and first reduction potential[a] of **16**–**28**.

Compound	λ_{max} (log ε)[b]	E_1^{red} [V]
16	560 (3.83)	−0.43
17	388 (4.27), 508 (4.32)	−0.64
18	401 (4.49), 420 sh (4.55), 510 sh (3.81), 548 sh (3.53), 690 sh(2.89), 771 (2.70)	−0.64
19	390 sh (4.11), 557 (3.85)	−0.50
20	409 (4.27), 452 sh (4.02), 513 sh (3.85), 552 sh (3.71)	−0.50
21	392 sh (4.09), 558 (3.84)	−0.40
22	409 (4.35), 510 (4.44)	−0.53
23	387 sh (4.50), 452 sh (4.43), 513 (4.50)	−0.53
24	407 (4.77), 534 sh (3.88), 700 (3.22), 765 sh (3.07)	−0.53
25	401 sh (4.22), 552 (4.12)	−0.48
26	405 (4.46), 494 (4.36)	−0.42
27	403 sh (4.57), 534 sh (4.12)	−0.31
28	404 sh (4.52), 500 nm (4.57)	−0.42

[a] Measured by CV; V versus Ag/$AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1} and internal reference (Fc/Fc^+ = +0.15 V); Half-wave potentials E^{red} = (E_{pc} + E_{pa})/2 on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] sh = shoulder peak.

6. 1-Azulenyl TCBDs with Polycyclic Aromatic Hydrocarbons

Interactions between AzTCBDs through the benzene, thiophene, and azulene cores were confirmed by spectroscopic and electrochemical analysis. AzTCBDs on polycyclic aromatic hydrocarbons (PAHs) are expected to show unique electronic interactions among the AzTCBD units within the molecule arising from their extended conjugations. In 2012, Diederich *et al*. reported the synthesis of corannulene derivatives with mono-, di-, tetra-, and penta(DAA-substituted)TCBDs.[46] They also revealed their redox behaviors, which were not influenced by the number of TCBD units on the corannulene core. Wang and co-workers demonstrated the synthesis and properties of tetra(DAA-substituted)TCBD and DCNQ connected to pyrene cores.[47] However, the influence of the number and substitution position of the TCBD units on pyrene on the spectroscopic and electrochemical properties was not investigated. Although these compounds are rare examples of TCBD and DCNQ derivatives directly connected to PAH cores, systematic studies regarding their spectroscopic and electrochemical properties have not been conducted. Therefore, we examined the effects of PAH cores (e.g., naphthalene, pyrene, and hexabenzocoronene) connected to 1-AzTCBD units in order to facilitate the construction of electronic materials with useful optical and redox properties.

UV/Vis of 1-AzTCBDs **29** and **30** with naphthalene cores (Figure 5) showed broad absorption bands at around 400 ~ 700 nm, arising from the ICT between the azulene and TCBD units.[48] Likewise, bis-1-AzTCBDs **31**−**34** also displayed broad absorption bands in the visible region, without a clear peak maxima in the region. Similar to the bis-1-AzTCBDs **23**−**28**, the extinction coefficients of bis-1-AzTCBDs **31**−**34** increased as compared to those of 1-AzTCBDs **29** and **30** as the number of 1-AzTCBD units on naphthalene ring increased.

1-AzTCBDs **29** and **30** exhibited two-step reduction waves in CV upon electrochemical reduction. The E_1^{red} of **29** (−0.54 V) was less negative than those of **30** (−0.62 V) and **1** (−0.61 V) probably because of the effective conjugation between the 1-AzTCBD unit and 1-naphthyl group, which lowered the LUMO level. Bis-1-AzTCBDs **31**−**34** (−0.45 ~ −0.54 V) exhibited less negative E_1^{red} values than **29** and **30**. Although bis-1-AzTCBDs have a symmetric structure, two TCBD units in the molecule are reduced in a step-wise fashion *via* electrochemical reaction, resulting in multiply-charged anionic species. These results reveal the presence of redox interactions between the two 1-AzTCBD units *via* the naphthalene spacer.

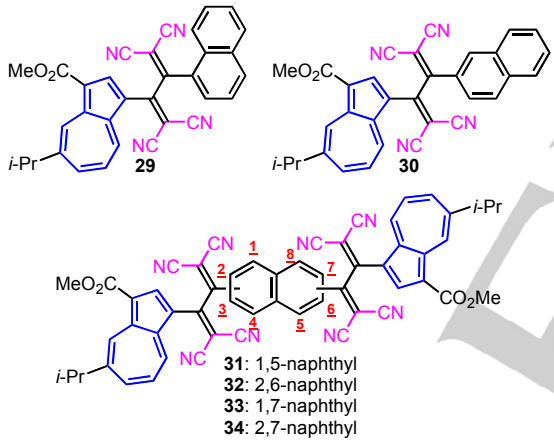


Figure 5. Structures of 1-AzTCBDs and bis-1-AzTCBDs **29**−**34** with naphthalene cores.

In order to investigate the electronic interactions between 1-AzTCBD units through the pyrene core, we examined the synthesis, spectroscopic, and electrochemical properties of 1-AzTCBD derivatives **35**−**37** containing pyrene cores (Figure 6).[49] Enlargement of the π-conjugated system typically led to the insolubility of the products in common organic solvents. Therefore, a *n*-hexyl ester group was introduced onto each azulene ring *via* transesterification in order to improve their solubility.

1-AzTCBDs **35**−**37** exhibited broad absorption bands in the visible region in their UV/Vis spectra. The molar extinction coefficient of **36** (λ_{max} = 510 nm, log ε = 4.38) was almost twice that of **35** (λ_{max} = 503 nm, log ε = 4.08), but the notable bathochromic shift of the longest wavelength absorption maximum was not observed in bis-1-AzTCBD **36**. Therefore, the electronic interaction between the two 1-AzTCBDs at the 1- and 6-positions is rather small through the central pyrene ring. On the other hand, the end absorption of **37** showed a clear bathochromic shift, which reached to the near-infrared region, compared with those of **35** and **36**. These results indicate that the conjugation (1- and 8-positions) or cross-conjugation (1- and 3-positions) between the two 1-AzTCBD units is involved in the expansion of the π-conjugated system.

1-AzTCBDs **35**−**37** exhibited multi-step reduction waves in CV. The voltammetry experiments showed that the first reduction potential became less negative as the number of 1-azulenyl TCBD units increased. In particular, the E_1^{red} of **37** (−0.35 V) showed a larger potential shift than those of **35** (−0.50 V) and **36** (−0.47 V). This could be explained by the interaction among the 1-AzTCBD substituents in the molecule, which lowered the LUMO level, making the electrochemical reduction more likely to occur.

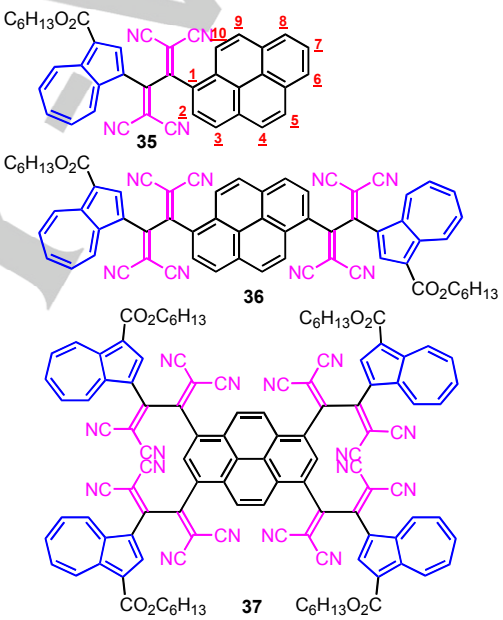


Figure 6. Structures of 1-AzTCBDs **35**−**37** with pyrene cores.

Hexabenzocoronene (HBC) is a PAH and is widely studied in the development of organic electronic materials.[50] However, the functionalization of HBC derivatives is difficult owing to their low solubility in organic solvents. Thus, synthesis of HBC derivative **38** and hexaphenylbenzene derivative **39** with six 1-AzTCBD units was accomplished using a similar procedure as that for the pyrene derivatives (Figure 7).[51] Specifically, the synthesis of 1-AzTCBD **38** was accomplished by the Sonogashira−Hagihara reaction of hexaiodo HBC[52] with a 1-ethynylazulene derivative, and followed by the [2 + 2] CA−RE with TCNE.

Compounds **38** and **39** showed broad absorptions in the visible region. HBC derivative **38** showed an absorption centered at 466 nm, which reached the near-infrared region.

This absorption band was not observed in hexaphenylbenzene derivative **39**. Thus, this absorption band was attributed to the transition of the HBC moiety. Although **38** and **39** showed two-step reduction waves, **38** (−0.58 V) showed a lower first reduction potential than **39** (−0.67 V). This was because the LUMO level decreased due to the intramolecular electronic interaction with the 1-AzTCBDs through the planar HBC core.

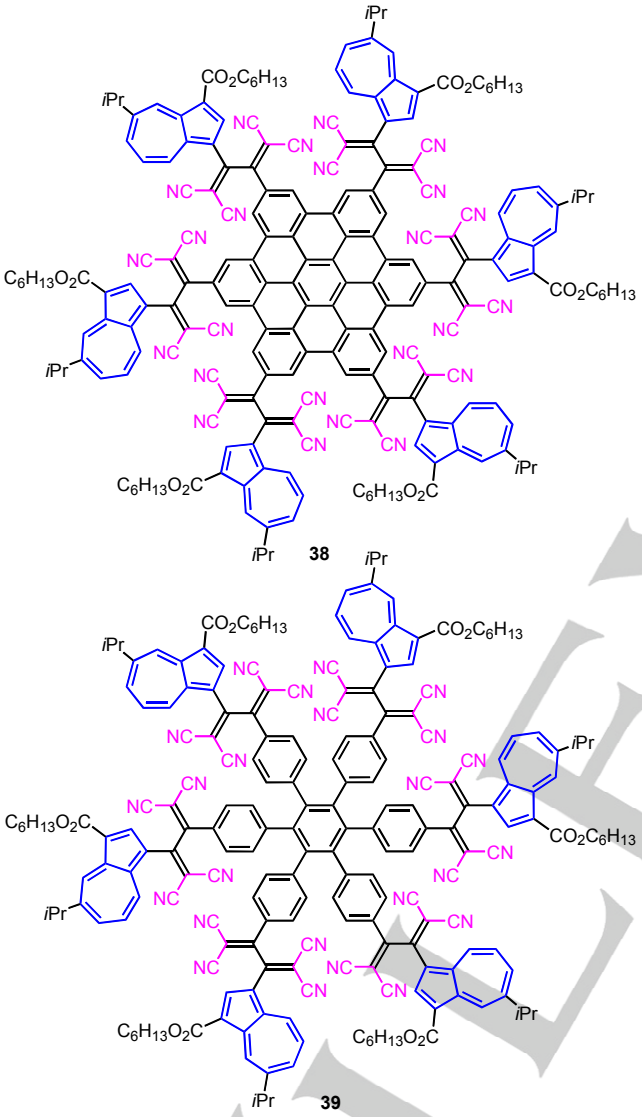


Figure 7. Structures of 1-AzTCBD **38** and **39** with hexabenzocoronene and hexaphenylbenzene cores.

7. 1-, 2-, and 6-Azulenyl TCBDs with Ferrocene Substituents

In 2002, Mochida *et al*. reported that ferrocene-substituted TCBD derivatives could be obtained by the reaction of ethynylferrocenes with TCNE. They also reported an amphoteric redox behavior.[29a] Since then, considerable attention has been devoted to the preparation of ferrocene-substituted TCBD derivatives bearing various π-electron systems to clarify their unique amphoteric redox behaviors.[29,53] To construct amphoteric multistage redox systems that show both reversible oxidation and reduction waves, we investigated the synthesis of AzTCBD derivatives with ferrocene substituents, as well as their optical and electrochemical properties. Preparation of ferrocene-substituted AzTCBDs **40**−**46** was accomplished by the [2 + 2] CA−RE of ferrocenylethynylazulene derivatives with TCNE (Figure 8).[XX] In this reaction, the ferrocene substituent on 2- and 6-ethynylazulenes acts as an activating group and accelerates the [2 + 2] CA−RE reaction.

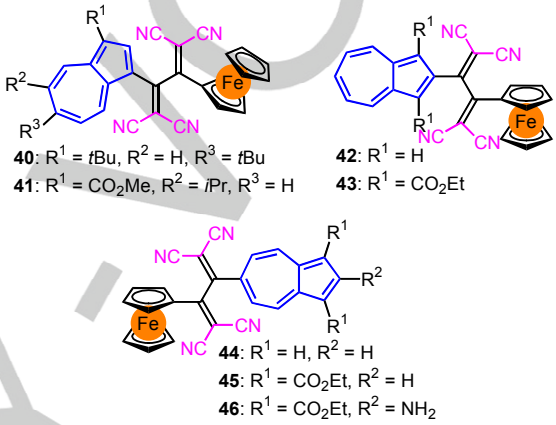


Figure 8. Structures of AzTCBDs **40**−**46** with ferrocene substituents.

In the visible region, AzTCBDs **40**−**46** exhibited a broad ICT absorption band that reached the near-infrared region, which arose from the d-d* transition of the ferrocene moiety.[55] The absorption band of **46** was ascribed to the quinoid resonance structure in the azulene moiety[43] in conjugation with the 2-amino group, similar to that of TCBDs **22** and **28**.

AzTCBD chromophores **40**−**46** showed one-stage oxidation waves originating from the oxidation of the ferrocenyl group. Since the oxidation potentials of the AzTCBD chromophores **40**−**46** were similar (E_1^{ox} = +0.56 ~ +0.61 V), the HOMO level of ferrocene was not affected by the position of the substituted azulenyl group (Table 4). On the other hand, the first reduction potential of **40**−**46** depended on the substituent and the substituted position in the azulene ring. The E_1^{red} of **40** (−0.85 V) was more negative than that of **41** (−0.77 V). The positive shift of the E_1^{red} of **43** (−0.59 V) and **45** (−0.52 V) as compared to those of **42** (−0.77 V) and **44** (−0.66 V) was ascribed to the two ethoxycarbonyl groups on the azulene ring in the 1,3-positions. The E_1^{red} of **46** (−0.66 V), which has an electron-withdrawing ethoxycarbonyl group in the 1,3-positions of the azulene ring, was almost the same as those of **44** and TCBDs **22** and **28** with 2-aminoazulene substituents. In summary, TCBDs **44**−**46** exhibited lower reduction potentials than TCBDs **40**−**43** because the 6-azulenyl substituent has a higher electron-accepting ability than the 1- and 2-azulenyl group.

The reversible color changes of **40**–**46** under electrochemical oxidation conditions were predictable owing to the generation of stable ferrocenium ions, but reversibility was not observed under the experimental conditions. These results may suggest that the ferrocenium ions produced by electrochemical oxidation were destabilized by the electron-withdrawing effect of the TCBD moiety. In contrast, significant spectral changes were observed for **40**–**46** under the constant-current reduction. For example, the electrochemical reduction of TCBD **43** gradually resulted in a new absorption band at 530 nm, along with a color change from light-green to purple. Upon electrochemical reduction, **45** gradually exhibited new absorption bands in the visible region at 510 nm and 610 nm, along with a color change from greenish-blue to yellow. The reverse oxidation of **43** and **45** led to the recovery of the original spectra and colors.

Table 4. Absorption maxima [nm] in the visible region, coefficients (log ε) in dichloromethane, and first oxidation and reduction potentials[a] of **40**–**46**.

Compound	λ_{max} (log ε)[b]	E_1^{ox} [V]	E_1^{red} [V]
40	492 (4.16), 590 sh (3.62)	+0.56	−0.85
41	459 (4.10), 644 sh (3.31)	+0.58	−0.77
42	402 (4.41), 427 sh (4.17), 616 (3.48)	+0.58	−0.77
43	556 (3.24), 753 (3.07)	+0.56	−0.59
44	394 sh (4.06), 638 (3.43)	+0.60	−0.66
45	380 sh (4.28), 621 (3.47)	+0.61	−0.52
46	408 sh (4.04), 499 (4.28), 640 sh (3.38)	+0.60	−0.66

[a] Measured by CV; V versus Ag/$AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1} and internal reference (Fc/Fc^+ = +0.15 V); Half-wave potentials E^{red} = (E_{pc} + E_{pa})/2 on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] sh = shoulder peak.

8. Heteroazulenyl TCBDs with Aryl Substituents

2H-cyclohepta[b]furan-2-one (CHF), a precursor for azulene derivatives, is a heteroazulene derivative.[56] However, there are few reports on the applications of such compounds in advanced materials. Thus, we investigated the preparation of new TCBDs based on CHFs for the construction of multistage redox active chromophores.[57]

Preparation of 3-ethynyl CHF derivatives was accomplished *via* Sonogashira–Hagihara coupling for the first time. Similar to TCBD derivatives with azulenyl substituents, CHF-substituted TCBDs **47**−**53** were obtained by the [2 + 2] CA−RE of the corresponding alkynes with TCNE (Figure 9). The alkynes also reacted with TCNQ[58] and DDQ[59] to afford the corresponding addition products. The CHF substituent on the alkyne acts as an activating group to promote the [2 + 2] CA−RE reaction, similar to 1-azulenyl groups.

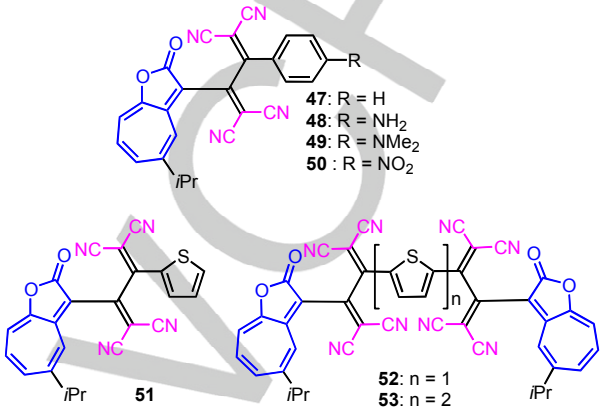


Figure 9. Structures of TCBDs **47**−**53** with CHF substituents.

Although the longest wavelength absorption maxima of **47**–**50** were similar (Table 5), the absorption coefficients of **48** (λ_{max} = 495 nm, log ε = 4.48) and **49** (λ_{max} = 491 nm, log ε = 4.51) in CH_2Cl_2 were twice as large as those of **47** (λ_{max} = 498 nm, log ε = 4.54) and **50** (λ_{max} = 499 nm, log ε = 4.21). These differences might be attributed to the conjugation between TCBD and the *para*-amino substituent on the benzene ring of **48** and **49**. The absorption coefficient of **52** (λ_{max} = 491 nm, log ε = 4.67) was almost twice that of **51** (λ_{max} = 494 nm, log ε = 4.42), although the absorption maxima appeared at similar wavelengths. The longest wavelength absorption (λ_{max} = 504 nm, log ε = 4.82) of **53** was red-shifted as compared to those of **51** and **52**, owing to the expanded π-conjugation, similar to the ferrocene-substituted TCBDs.[60]

The TCBD chromophores displayed multi-step reduction waves in CV. Particularly, TCBD **50** showed four-step reduction waves, which were ascribed to the formation of a tetraanionic species due to the electron affinity of the p-nitrobenzene group on TCBD. Moreover, the E_1^{red} of **50** (−0.05 V) was less negative than those of **47** (−0.51 V), **48** (−0.65 V), and **49** (−0.67 V), owing to the *p*-nitrobenzene substituent on TCBD, which is a strong electron-withdrawing group (Table 5).

When the spectral changes of bis-TCBD **52** were measured under electrochemical reduction conditions, a new absorption band at around 635 nm developed and extended into the near-infrared region, owing to the generation of anionic species of **52**. Reverse oxidation resulted in a decrease in the new absorption band, along with the recovery of the original spectrum of **52**. Similar to bis-1-AzTCBD **5**, the reversible color changes of **52** were attributed to the violene-cyanine-violene moiety.[34]

Table 5. Absorption maxima [nm] in the visible region, coefficients (log ε) in

dichloromethane, and first reduction potential[a] of **47**–**53**.

Compound	λ_{max} (log ε)	E_1^{red} [V]
47	498 (4.27)	−0.51
48	495 (4.48)	−0.65
49	491 (4.54)	−0.67
50	499 (4.21)	−0.05
51	494 (4.42)	−0.55
52	491 (4.67)	−0.29
53	504 (4.82)	−0.46

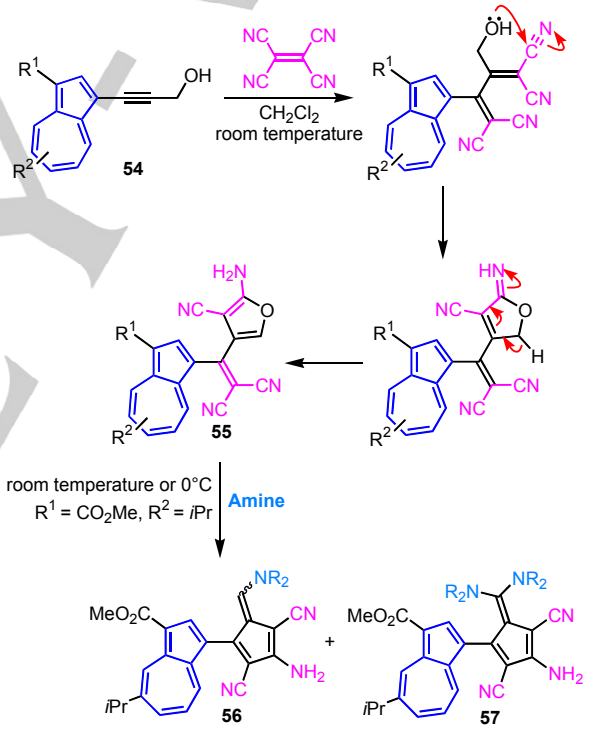
[a] Measured by CV; V versus Ag/$AgNO_3$, 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1} and internal reference (Fc/Fc^+ = +0.15 V); Half-wave potentials $E^{red} = (E_{pc} + E_{pa})/2$ on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

9. 2-Aminofuran Derivatives with 1-Dicyanovinylazulenes and Transformation into 6-Aminofulvenes Substituted with Azulenyl Groups

Aminofuran derivatives exhibit various biological activities and are found in many pharmaceuticals.[61] Therefore, general and efficient synthetic methods have been developed for these derivatives. Upon exploring reactions for the synthesis of new TCBDs, we unexpectedly discovered the generation of 2-aminofuran derivatives by the [2 + 2] CA−RE reaction of 3-(1-azulenyl)propargyl alcohols with TCNE (Scheme 8).[62] As illustrated in Scheme 8, the formation of a TCBD intermediate was expected upon reaction of **54** with TCNE. The intramolecular nucleophilic addition of the hydroxyl group to the cyano moiety gives the dihydrofuran derivative from the TCBD intermediate, which then tautomerizes to form a furan ring. It should be noted that the nature of functional groups R^1 and R^2 on the azulene ring had little influence on the formation of the 2-aminofuran derivatives, since the reaction produced the products in good to excellent yields (61−99%).

The 2-aminofuran derivatives exhibited strong absorption bands in the visible region, and the absorption maxima of these compounds largely depended on the substituents on the azulene ring. DFT calculations at the B3LYP/6-31G** level revealed that the strong absorption bands of **55** could be assigned to an ICT between the HOMOs, which were located on the azulene and 2-aminofuran moieties, and the LUMOs, which were mainly located on the azulene and dicyanovinyl groups.

6-Aminopentafulvenes have typically been prepared from cyclopentadienide ions with the corresponding amides or their analogues.[63] We discovered the unexpected formation of 6-aminopentafulvene derivatives while investigating the reactivity of 2-aminofuran derivatives **55** with various amines. When 2-aminofuran derivatives **55** with an azulenyl substituent were treated with an excess of primary and secondary amines, 6-aminopentafulvenes **56** were obtained in 16−98% yields. However, the use of sterically bulky amines (i.e., diisopropylamine and *tert*-butylamine) resulted in low product yields (diisopropylamine, 16%; *tert*-butylamine, 41%) due to the prevention of the nucleophilic addition of the amine on the furan ring. When highly nucleophilic amines (i.e., piperidine and pyrrolidine) were employed, 6,6-diaminopentafulvene derivatives **57** were also generated. This procedure was the first example of the preparation of 6-aminopentafulvene derivatives from 2-aminofurans by an amine-induced transformation, without the use of cyclopentadienide ion.



Scheme 8. Synthesis of 2-aminofuran derivatives with 1-dicyanovinylazulenes **55** and transformation into 6-aminofulvenes **56** and **57**.

10. Conclusion

We have demonstrated the preparation and properties of 1-AzTCBDs with various π-electron systems, as well as CHF-substituted TCBDs. TCBD derivatives were prepared by the formal [2 + 2] CA of the corresponding alkyne derivatives with TCNE, followed by the RE of the initially formed cyclobutene derivatives. Since the [2 + 2] CA−RE does not proceed with 2- and 6-ethynylazulene derivatives, the reaction requires an

activating electron-donating group on the alkyne moiety. Although the details are omitted in this article, TCNQ also reacts with the electron-rich alkynes to produce the corresponding DCNQs. In the case of the reaction with 3-(1-azulenyl)propargyl alcohols, the [2 + 2] CA−RE with TCNE and the intramolecular nucleophilic addition proceed to form 2-aminofuran derivatives. The obtained 2-aminofuran derivatives can be transformed into 6-aminofulvene derivatives with a 1-azulenyl substituent.

The ICT characteristics of 1-AzTCBDs were revealed by UV/Vis spectroscopic analysis. In most cases, bathochromic shifts and increases in the extinction coefficients were observed with increasing numbers of 1-AzTCBD units on the π-electron systems.

1-AzTCBDs exhibited multi-step reduction waves in CV. The first reduction potential depended on the π-electron system and the substituent connected to the 1-AzTCBD unit. Therefore, the redox potential can be controlled by the substituent on the π-electron system connected to the 1-AzTCBD unit. Furthermore, 1-AzTCBDs with C_2 and C_3 symmetry (e.g., **2**, **3**, **5**, **8**−**10**, and **23**−**28** among others) exhibit multi-step reduction waves, since the TCBD units are reduced step-wise. These results suggest the presence of electronic interactions among 1-AzTCBD units in the molecule through the connected π-electron systems. Although some issues remain in regard to the reversibility for practical use in electrochromic devices, most 1-AzTCBDs show spectral and color changes under electrochemical reduction conditions owing to the generation of anionic species. TCBD derivatives bearing both 1-azulenyl and 2- or 6-azulenyl groups display reversible and remarkable color changes under redox conditions, owing to the stabilization of radical ions and/or ionic states generated by the electrochemical redox reaction, while TCBDs with only 1-azulenyl groups do not.

The use of AzTCBD units as redox active chromophores is very attractive for applications in organic electronic materials, especially electrochromic materials, because 1-AzTCBDs exhibit high redox activity with multistage redox behavior, the ability to stabilize anionic states, and large absorptions in the visible region. Novel organic electronic materials with useful and interesting functions will be developed by utilizing the unique properties of the AzTCBDs.

Acknowledgements

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Keywords: azulene • heteroazulene • donor-acceptor system • cycloaddition • redox chemistry

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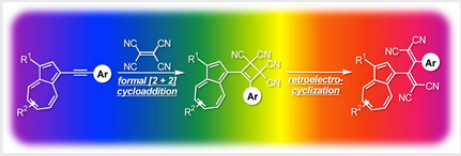
CONCEPT



Herein, we describe the synthesis and properties of azulene-substituted 1,1,4,4-tetracyanobutadienes (AzTCBDs), as well as those of heteroazulenyl TCBDs. TCBD derivatives were prepared by the reaction of the corresponding 1-ethynylazulenes with tetracyanoethylene (TCNE). In contrast, the reaction of propargyl alcohols with the 1-azulenyl group on TCNE generated unexpected 2-aminofuran derivatives, which were transformed into 6-aminofulvenes upon treatment with several amines. The optical and electrochemical properties of the AzTCBDs were clarified by UV/Vis and cyclic voltammetry.

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