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PAPER

Synthesis of donor–acceptor chromophores by the [2 + 2] cycloaddition of arylethynyl-2*H*-cyclohepta[*b*]furan-2-ones with 7,7,8,8-tetracyanoquinodimethane†

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Arylethynyl-2*H*-cyclohepta[*b*]furan-2-ones reacted with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a formal [2 + 2] cycloaddition reaction, followed by ring opening of the initially formed cyclobutene derivatives, to afford the corresponding dicyanoquinodimethane (DCNQ) chromophores in excellent yields. The intramolecular charge-transfer (ICT) interactions between the 2*H*-cyclohepta[*b*]furan-2-one ring and DCNQ acceptor moiety were investigated by UV/Vis spectroscopy and theoretical calculations. The redox behavior of the novel DCNQ derivatives was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which revealed their multistep electrochemical reduction properties depended on the number of DCNQ units in the molecule. Moreover, a significant color change was observed by visible spectroscopy under electrochemical reduction conditions.

Introduction

Charge-transfer (CT) materials composed of an organic donor–acceptor system have been intensively studied because of their potential for applications in organic electronic devices in the next generation. Cyano-based acceptor is one of the most promising units for application in organic electronic devices within a large number of organic acceptors previously reported.[1] Tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) are well known as powerful electron acceptors to form CT complexes with a variety of electron-rich organic and organometallic compounds.[2] The CT complexes are revealed to exhibit a number of interesting properties such as electric conductivity,[3] which is a very promising feature for application in optoelectronic devices (*e.g.*, organic light-emitting diodes and solar cells).[4]

Diederich *et al.* have reported the synthesis of intramolecular charge-transfer (ICT) chromophores, donor-substituted 1,1,2,2-tetracyanobutadienes (TCBDs) and dicyanoquinodimethanes (DCNQs) by the formal [2 + 2] cycloaddition, followed by ring-opening cycloreversion of the initially formed cyclobutene derivatives, of TCNE[5] and TCNQ[6] with a variety of alkynes bearing an electron-donating substituent (*e.g.*, *N*,*N*-dialkylaniline, ferrocene, and tetrathiafulvalene substituents). These compounds are revealed to show the intense ICT absorptions on their UV/Vis spectra. Furthermore, the ICT chromophores are expected to show optical non-linearities[7] and their utilities as organic-base magnets and conductive materials are proved.[5,6]

Li *et al.* have also reported the synthesis and properties of donor-acceptor substituted π-conjugated system by cycloaddition-reversion sequence reaction of acetylene with TCNE and TCNQ.[8]

Michinobu *et al.* have extended this class of chemistry to the polymer science.[9] They reported the TCBD and DCNQ-embedded polymer materials to show the ICT absorption bands with the low energy band gap. Moreover, these polymers are expected to be promising materials for semiconductors in organic photovoltaic devices,[9a] nonlinear optical applications[9c] and ion sensors.[9i]

Recently, we have reported the reaction of mono-, bis-, and tris(1-azulenylethynyl)benzene and thiophene derivatives with TCNE[10] and TCNQ[11] to give the corresponding azulene-substituted TCBD and DCNQ derivatives as redox active ICT chromophores, which revealed their electrochromic behavior to show significant color changes under electrochemical reduction conditions. Therefore, from the viewpoint of the development of organic electronics, construction of a new series of donor–acceptor systems composed of cyano-based acceptors is one of the most attractive targets in current organic chemistry.

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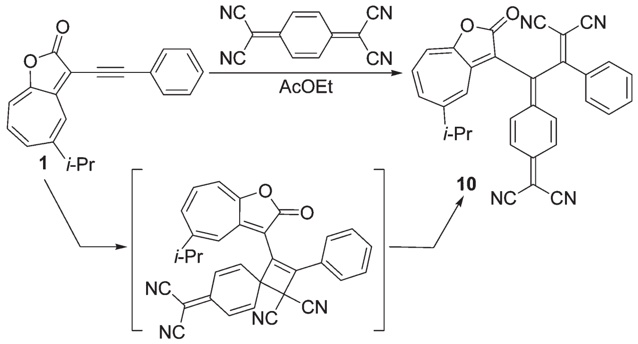
2*H*-Cyclohepta[*b*]furan-2-one is well known as a heteroazulene, a versatile precursor for azulene derivatives.[12] For the extension of this chemistry, we have focused our attention on the synthesis of 2*H*-cyclohepta[*b*]furan-2-one-substituted TCBD derivatives by the reaction of the corresponding alkynes with TCNE.[13] The study revealed the TCBD derivatives feature a strong ICT absorption in their UV/Vis spectra, which is characterized by time-dependent density functional theory (TD-DFT) calculations. Reaction of arylethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1–9** with TCNQ is expected to show high reactivity toward the formal [2 + 2] cycloaddition–cycloreversion sequence to afford the novel DCNQ derivatives. Moreover, 2*H*-cyclohepta[*b*]furan-2-one-substituted DCNQs should also exhibit multistage redox behavior, similar to the TCBD derivatives. Moreover, a significant color change is also expected during the electrochemical reduction of the DCNQ derivatives.

Herein, we describe the synthesis of the 2*H*-cyclohepta[*b*]furan-2-one-substituted DCNQs by the reaction of arylethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1–9** with TCNQ. Electronic properties of the novel donor–acceptor systems are characterized by absorption spectroscopy, theoretical calculations, cyclic voltammetry (CV), and differential pulse voltammetry (DPV). The data confirm the ICT characters of the novel donor–acceptor systems with their electrochromic property.

Results and discussion

Synthesis

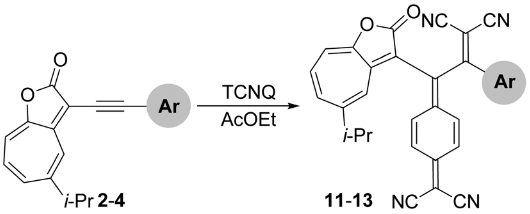
The arylethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1–9** were prepared by Sonogashira–Hagihara reactions, according to the procedure reported by us, recently.[13] To the synthesis of the novel DCNQ derivatives, the [2 + 2] cycloaddition–cycloreversion sequence was applied to the acetylene derivatives **1–9** with TCNQ under the conditions described in the literature.[6,11] Thus, the reaction of **1** with TCNQ in refluxing ethyl acetate afforded **10** in 91% yield as a sole product (Scheme 1). Proposed reaction sequence is also shown in Scheme 1. The reaction commences with the formal [2 + 2] cycloaddition between the exocyclic C=C double bond of TCNQ and the alkyne moiety of **1**, followed by the ring opening of the intermediately formed strained cyclobutene derivative to give **10** as shown in the parentheses.



Scheme 1 Presumed reaction mechanism for [2 + 2] cycloaddition of **1** with TCNQ.

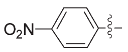
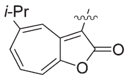
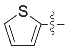
The electronically more deficient alkyne **2**, which has *p*-nitro-substituent on the benzene ring, also reacted with TCNQ to afford **11** in 90% yield (Scheme 2, Table 1, entry 1), although the relatively longer reaction period was required in this case (24 hours). Recently, we have reported the reaction of **2** with TCNE, which completed within 2 hours.[13] Diederich *et al.* have also reported that TCNQ shows lower reactivity, compared with TCNE, towards the formal [2 + 2] cycloaddition reaction with electron-deficient cyanoalkynes.[6b] Furthermore, they have also reported that excess of TCNQ, prolonged reaction period, and elevated temperature are required to complete the reaction with the alkynes substituted with a strong electron-withdrawing group. Therefore, the relatively longer reaction period in the reaction of **2** also reflects the lower reactivity of TCNQ toward such electron deficient alkynes. The new chromophore **12** was also obtained in 92% yield by the formal [2 + 2] cycloaddition–cycloreversion sequence between TCNQ and electron-rich alkyne **3** (Table 1, entry 2). The reaction of **4** with TCNQ in refluxing ethyl acetate afforded the corresponding product **13** in 91% yield (Table 1, entry 3).

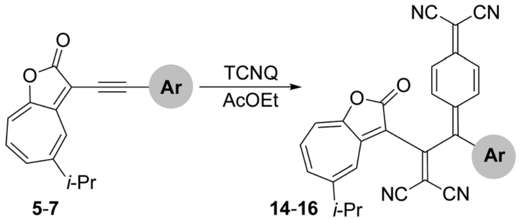
For the reaction of **5** with TCNQ, compound **14**, with different regiochemistry shown in Scheme 3, was obtained in 87% yield (Table 2, entry 1). The reaction of ferrocene- and azulene-



Scheme 2 Reaction of 2*H*-cyclohepta[*b*]furan-2-one derivatives **2–4** with TCNQ.

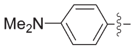
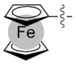
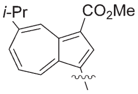
Table 1 Synthesis of TCNQ-adducts with 2*H*-cyclohepta[*b*]furan-2-one substituents **11–13**

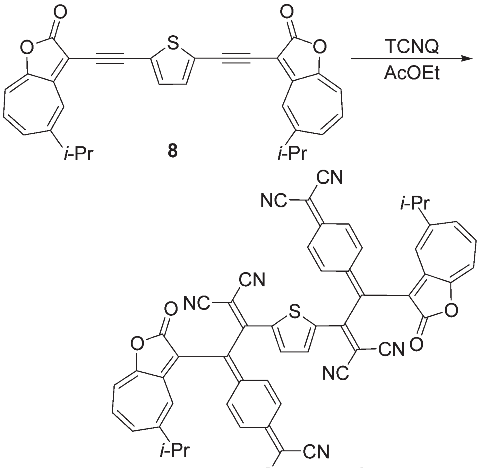
Entry	Substrate	Ar	Product	Yield [%]
1	**2**		**11**	90
2	**3**		**12**	92
3	**4**		**13**	91



Scheme 3 Reaction of 2*H*-cyclohepta[*b*]furan-2-one derivatives **5–7** with TCNQ.

Table 2 Synthesis of TCNQ-adducts with 2*H*-cyclohepta[*b*]furan-2-one substituents **14–16**

Entry	Substrate	Ar	Product	Yield [%]
1	**5**		**14**	87
2	**6**		**15**	98
3	**7**		**16**	97



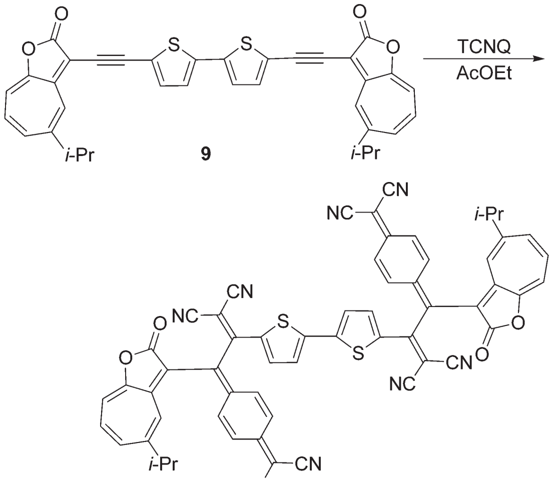
Scheme 4 Reaction of 2*H*-cyclohepta[*b*]furan-2-one derivative **8** with TCNQ.

substituted alkynes **6** and **7** with TCNQ afforded DCNQ derivatives **15** (98%) and **16** (97%), respectively (Table 2, entries 2 and 3). The difference in the regiochemistry of **14**, **15** and **16** might be reflected by the higher electron-donating property of *N*,*N*-dimethylaniline, ferrocene, and azulene moieties than that of the 2*H*-cyclohepta[*b*]furan-2-one unit.[6f]

Thiophene and bithiophene substituted DCNQ chromophores **17** and **18** were also obtained by the reaction of alkynes **8** and **9** with TCNQ in excellent yields (**17**: 92% and **18**: 96%), although a relatively longer reaction period was required to complete the reactions (Schemes 4 and 5). The lower reactivity of **8** and **9** might be explained by the deactivation of the alkyne moiety by the DCNQ unit generated by an addition of a TCNQ molecule within the two acetylene units in the molecule. These new DCNQ chromophores **10–18** are stable, deep-colored crystals, and storable in crystalline state at ambient temperature under aerobic conditions, likewise the corresponding 2*H*-cyclohepta[*b*]furan-2-one-substituted TCBD chromophores.

UV/Vis spectroscopy

UV/Vis spectra of DCNQs **10** in dichloromethane and hexane including dichloromethane are shown in Fig. 1. UV/Vis spectra of the other DCNQs **11–18** are summarized in the ESI.† The absorption maxima (λ_{max}) and their coefficients (log ε) of DCNQs **10–18** are shown in Table 3. Most of the DCNQ chromophores showed intense ICT absorption bands in the visible region. Solvatochromism was also observed as a characteristic feature of these molecules.[14] The distinct absorption band of **10** at 615 nm in CH_2Cl_2 exhibits blue shift by 27 nm in the less polar 10% CH_2Cl_2–hexane, which suggests the ICT nature of this band (Fig. 1). The shift value of **10** (27 nm) is larger than that of the corresponding TCNE-adduct of **1** (6 nm).[13] These results assume that the first excited-state has a larger dipole moment compared with that in the ground state, due to the effective ICT character from 2*H*-cyclohepta[*b*]furan-2-one to the DCNQ unit.



Scheme 5 Reaction of 2*H*-cyclohepta[*b*]furan-2-one derivative **9** with TCNQ.

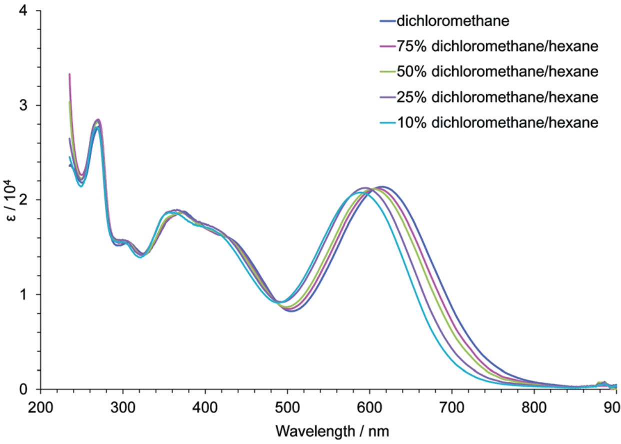


Fig. 1 UV/Vis spectra of **10** in dichloromethane and in dichloromethane–hexane.

The solvent dependence of the absorption maxima and coefficients (log ε) of **10** are summarized in Table 4. The UV/Vis spectra of DCNQs **10** in each solvent are shown in the ESI.† The largest solvent effect was observed when the solvent was changed from acetonitrile (λ_{max} = 617 nm) to 10% CH_2Cl_2–hexane (λ_{max} = 588 nm).

Similar with **10**, compounds **11** and **14** showed a broad ICT absorption band at 626 nm and 718 nm in CH_2Cl_2, respectively.

Table 3 Absorption maxima [nm] and their coefficients (log ε) of DCNQ chromophores **10–18** in dichloromethane and in 10% CH_2Cl_2/hexane

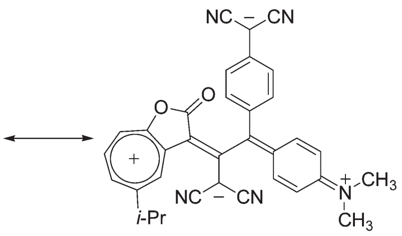
Sample	λ_{max} (log ε) in CH_2Cl_2	λ_{max} (log ε) in hexane[a]
10	615 (4.44)	588 (4.35)
11	626 (4.33)	597 (4.32)
12	624 (4.49)	590 (4.49)
13	607 (4.48)	585 (4.39)
14	496 (4.43), 718 (4.46)	480 (4.41), 657 (4.46)
15	590 (4.40)	573 (4.36)
16	653 (4.35)	604 (4.31)
17	597 (4.77)	635 (4.53)
18	602 (4.70)	600 (4.59)

[a] Dichloromethane (10%) was included to keep the solubility of these compounds.

Table 4 Solvatochromic data for the longest wavelength absorption of **10**

Solvent	λ_{max} (log ε)	Solvent	λ_{max} (log ε)
MeCN	617 (4.29)	$CHCl_3$	610 (4.33)
CH_2Cl_2	615 (4.33)	AcOEt	605 (4.27)
THF	615 (4.32)	10% CH_2Cl_2/hexane	588 (4.35)

14



Scheme 6 Presumed resonance structure of **14**.

In these cases, the longest wavelength absorption maxima also exhibited hypsochromic shift in 10% CH_2Cl_2–hexane (**11**: 597 nm and **14**: 657 nm). Although the longest wavelength absorption of **10** and **11** are observed in an almost similar spectral region, compound **14** in CH_2Cl_2 showed bathochromic shift by about 100 nm compared with those of **10**, **11** and **13**. The large shift might be ascribed to the considerable contribution of the conjugation between *N*,*N*-dimethylaniline and DCNQ moieties as illustrated in Scheme 6.

The DCNQ chromophores **12**, **15** and **16** exhibited a strong and broad ICT absorption band at 624 nm, 590 nm and 653 nm in CH_2Cl_2, respectively. Whereas the longest wavelength absorption maximum of **12** in the spectral region is resembled with those of **10** and **11**, absorption maxima of **15** and **16** in CH_2Cl_2 exhibit considerable hypsochromic and bathochromic shifts, respectively. These results might be attributed to the effectiveness of the ICT between the DCNQ unit and directly conjugated ferrocenyl and 1-azulenyl groups, rather than the cross conjugation with the 2*H*-cyclohepta[*b*]furan-2-one ring.

The larger absorption coefficient was displayed by the ICT absorption bands of bis-adducts **17** and **18**, compared with that of mono-adduct **13**. The spectrum of **17** displayed an ICT absorption band (λ_{max} = 597 nm, log ε = 4.77 in CH_2Cl_2). The coefficient of **17** was almost twice as large as that of **13** (λ_{max} = 607 nm, log ε = 4.48 in CH_2Cl_2), although the absorption maximum showed blue-shift by 10 nm compared with that of **13**. Bis-adduct **18** also exhibited an intense and broad ICT absorption band (λ_{max} = 602 nm, log ε = 4.70 in CH_2Cl_2) as similar with **17**, but exhibited bathochromic shift by 5 nm relative to that of **17** probably due to the results on the extension of π-electron system by bithiophene unit.

Table 5 Electronic transitions for **10′** and **12′** derived from the computed values based on B3LYP/6-31G** method and experimental values from **10** and **12**

Sample	Experimental λ_{max} (log ε)	Computed value λ_{max}	Strength	Composition of band[a,b]
10′	**10**, 615 (4.44)	559	0.4374	H − 1 → L (−0.54) H → L (0.76) H → L + 2 (−0.27)
12′	**12**, 624 (4.49)	585	0.1888	H − 1 → L (0.63) H → L (−0.50) H → L + 1 (−0.56)

[a] H = HOMO; L = LUMO. [b] The values in the parentheses are the configuration interaction (CI) coefficients.

To elucidate the nature of the absorption bands of **10** and **12**, TD-DFT calculation at the B3LYP/6-31G** level[15] are carried out as model compounds **10′** and **12′**, where isopropyl groups in **10** and **12** are replaced by H-groups. The frontier Kohn–Sham orbitals of these compounds are shown in the ESI.† Judging from the comparison between the experimental and the theoretical UV/Vis spectra, absorption maxima of **10** and **12** were assignable to overlaps of some transitions (Table 5).

The ICT of **10′** occurred from the HOMO located on 2*H*-cyclohepta[*b*]furan-2-one and HOMO − 1 located at the benzene ring to the LUMO located on DCNQ moiety and LUMO + 2 which are mainly located on the dicyanovinyl (DCV) group, although the contribution of the transitions for HOMO − 1 → LUMO and HOMO → LUMO + 2 is relatively low. Whereas, the ICT of **12′** confirmed that the longest absorption band arisen from the overlapping of HOMO − 1 → LUMO, HOMO → LUMO and HOMO → LUMO + 1. Different from the results on **10′**, contribution of HOMO → LUMO (*i.e.*, transition between attached 2*H*-cyclohepta[*b*]furan-2-one and DCNQ moieties), is less effective than that of detached 2*H*-cyclohepta[*b*]furan-2-one to DCNQ. The red-shift of the absorption for **12** might be attributable to the expansion of π-electron system by the cross-conjugated DCV moiety.

Electrochemistry

To clarify the electrochemical properties, the redox behavior of DCNQ chromophores **10–18** was examined by CV and DPV. Measurements were carried out with a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte with platinum wire and disk as auxiliary and working electrodes, respectively. All measurements were carried out under an argon atmosphere, and potentials were related to an Ag/Ag^+ reference electrode and

Table 6 Redox potentials of DCNQ chromophores **10–18**[a]

Sample	Method	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]
10	CV	−0.37	−0.53	
	(DPV)	(−0.35)	(−0.51)	
11	CV	−0.29	−0.43	
	(DPV)	(−0.27)	(−0.41)	(−1.46)[b]
12	CV	−0.38	−0.49	
	(DPV)	(−0.36)	(−0.47)	(−1.92)
13	CV	−0.42	−0.50	
	(DPV)	(−0.40)	(−0.48)	
14	CV	−0.47	−0.58	
	(DPV)	(−0.45)	(−0.58)	(−1.73)
15	CV	−0.49	−0.62	
	(DPV)	(−0.47)	(−0.60)	
16	CV	−0.42	−0.57	
	(DPV)	(−0.40)	(−0.55)	(−1.92)
17	CV	−0.26	−0.37	−0.52 (2e)
	(DPV)	(−0.24)	(−0.35)	(−0.50)[c]
18	CV	−0.50 (4e)		
	(DPV)	(−0.36)	(−0.48)	

[a] Redox potentials were measured by CV and DPV [V *vs.* Ag/AgNO$_3$, 1 mM in benzonitrile containing Et$_4$NClO$_4$ (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mV s^{-1}, and Fc/Fc+ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses. [b] The E_4^{red} was observed at −1.80 V on DPV. [c] The E_4^{red} was observed at −1.77 V on DPV.

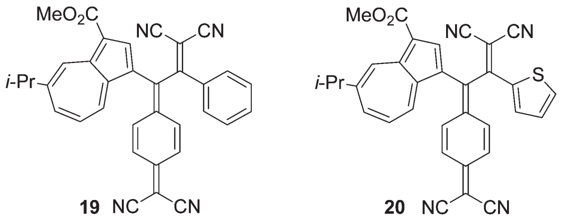
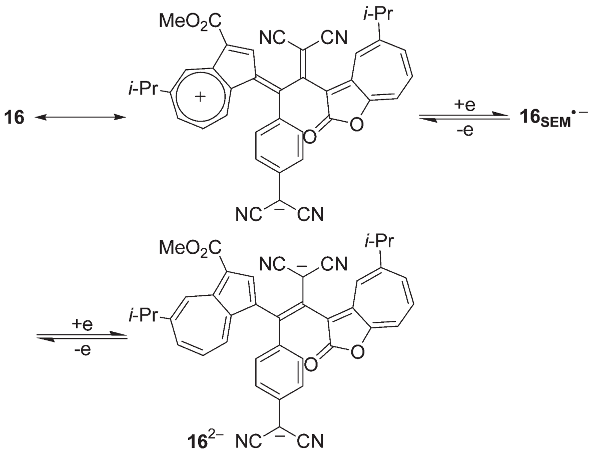


Fig. 2 TCNQ-adducts with 1-azulenyl substituent **19** and **20**.



Scheme 7 Presumed electrochemical behavior of **16**.

Fc/Fc$^+$ as an internal reference, which discharges at +0.15 V. The redox potentials (in volts *vs.* Ag/AgNO$_3$) of **10–18** are summarized in Table 6.

Electrochemical reduction of DCNQs **10**, **11** and **14** on CV exhibited a two-stage wave, but the first reduction potentials are varied to each other. The DCNQ with phenyl substituent **10** showed the reduction waves at −0.37 V and −0.53 V on CV. A positive shift of the first reduction potential was observed in **11** (−0.29 V) because of the substitution of the electron-withdrawing *p*-nitrophenyl group, which directly reflects the LUMO level of the molecules. In contrast, electrochemical reduction of **14** was featured by a negative shift of the first reduction potential (−0.47 V) owing to the *N*,*N*-dimethylaniline substituent with strong electron-donating nature.

The compounds **12**, **15** and **16** showed a reversible two-stage wave composed of two one-electron transfer processes. The reduction potentials of **12** were identified as −0.38 V and −0.49 V on CV. Ferrocene-substituted DCNQ **15** also showed a reversible two-step wave at the half-wave potentials of −0.49 V and −0.62 V on CV, probably due to the formation of a radical anionic and a dianionic species, respectively. Reversible one-step oxidation wave centered at +0.46 V was also observed on CV, which can be ascribed to the oxidation of the ferrocene moiety. The oxidation potential of **15** is much more positive compared with that of the parent ferrocene (+0.15 V). It could be ascribed to effects on the electron-withdrawing DCNQ moiety substituted. The azulene-substituted DCNQ **16** exhibited a reversible two-step reduction wave, the potentials of which were identified by CV as −0.42 V and −0.57 V, to form a radical anionic and a dianionic species. Recently, we have reported the reduction potentials of the compounds **19** and **20** (**19**: E_1^{red} = −0.43 V, E_2^{red} = −0.59 V and **20**: E_1^{red} = −0.44 V, E_2^{red} = −0.58 V) (Fig. 2).[11] Since the values are consistent with those of **16**, 2*H*-cyclohepta[*b*]furan-2-one substituent contributes less effectively for electrochemical reduction compared with 1-azulenyl moiety as shown in Scheme 7. Thus, the first reduction potential of these compounds might depend on the 1-azulenyl substituent.

Similar to the electrochemical reduction of compounds **10–12** and **14–16**, that of DCNQ with thiophene substituent **13** showed a reversible two-stage reduction wave on CV (−0.42 V and −0.50 V) attributed to the formation of a dianionic species. A reversible three-stage wave was observed in bis-adduct **17** on CV (−0.26 V, −0.37 V and −0.52 V), in which the third reduction wave could be concluded to be a two-electron transfer in one step to form a tetraanionic species (Fig. 3). The electrochemical reduction of bithiophene derivative **18** showed a reversible one-stage broad reduction wave on CV centered at −0.50 V, which was identified as two waves at −0.36 V and −0.48 V by DPV, probably due to the formation of a tetraanionic species. For the series of electrochemical reductions of thiophene derivatives **13**, **17** and **18**, introduction of the two DCNQ units into the thiophene core results in large shifts of the first reduction potentials (*i.e.*, **13**: −0.40 V, **17**: −0.24 V and **18**: −0.36 V on DPV).

On the whole, the novel DCNQ chromophores **10–18** exhibit negative reduction potential compared with those of the corresponding TCBD chromophores, except for **11**. These results are attributable to the higher electron-accepting nature of the DCNQ moieties than that of the corresponding TCBD derivatives reported by us, recently.[13]

We have reported the synthesis of redox-active chromophores with the aim of the creation of stabilized electrochromic materials.[16] As a part of this study, we have also reported 2*H*-cyclohepta[*b*]furan-2-one-substituted TCBDs[13] and azulene-substituted TCBDs[10] and DCNQs,[11] in which we identified some

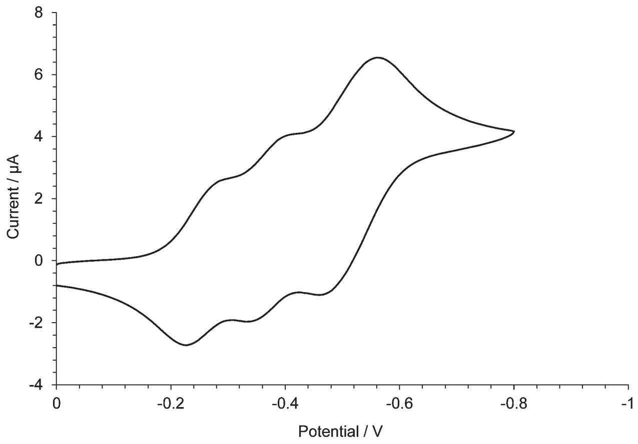


Fig. 3 Cyclic voltammograms of the reduction of **17** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{-1}.

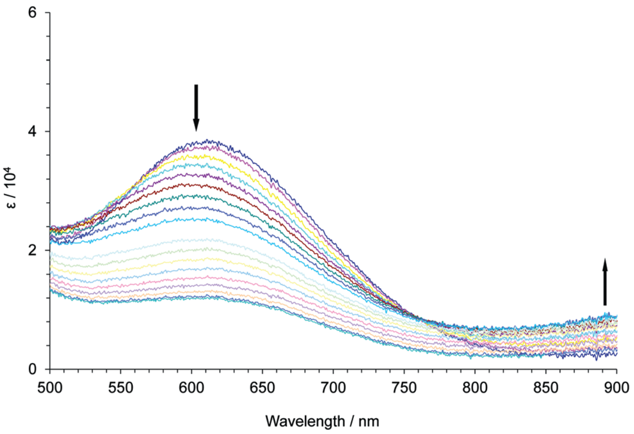


Fig. 4 Continuous change in the visible spectrum of **17**: constant-current electrochemical reduction (100 µA) in benzonitrile containing Et_4NClO_4 (0.1 M) at 30 sec intervals.

novel hybrid structures of violenes and cyanines[17] with the redox activities. Bis(2*H*-cyclohepta[*b*]furan-2-one-substituted) and bis(azulene-substituted) TCBDs, which exhibit reversible color changes during the electrochemical reaction, are successful examples of an extension of the violene–violene hybrid structure.[17] Similar to 2*H*-cyclohepta[*b*]furan-2-one-substituted TCBDs, 2*H*-cyclohepta[*b*]furan-2-one-substituted DCNQs **10–18** might exemplify the redox system for the extensions of the violene–violene hybrid system with multiple electron transfer. Thus, visible spectra of DCNDs **10–18** were monitored to clarify the color changes during the electrochemical reactions.

A constant-current reduction was applied to the solutions of **10–18** with a platinum mesh as the working electrode and a wire counter electrode. Visible spectra were measured in degassed benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte at room temperature under electrochemical reduction conditions (see the ESI†). The longest absorption of **10** at around 600 nm gradually decreased and thus the color of the solution gradually changed from greenish-blue to pale yellow during the electrochemical reduction, but reverse oxidation of the pale yellow-colored solution did not regenerate the spectrum of **10**, although good reversibility was observed in the two-step reduction on CV. The poor reversibility of the color changes might be attributable to the instability of the presumed dianionic species under the conditions for spectral measurements.

The longest absorption of **14** gradually decreased, and the color of the solution changed from dark-purple to yellow during the electrochemical reduction. However, reversible oxidation of the yellow-colored solutions did not regenerate the spectra of the corresponding original compound, completely. Vis spectra of **11** were measured under electrochemical reduction conditions, absorption of **11** in the visible region gradually decreased along with color change from green to yellow. Reverse oxidation did not regenerate the original absorption of **11**, although the comparative TCNE-adduct of **2** shows good reversibility on the spectral changes. When Vis spectra of **12** were measured under electrochemical reduction conditions, absorption of **12** in the visible region at around 620 nm gradually decreased. Reverse oxidation decreased the new absorptions, but did not regenerate the absorption of **12**, completely. The greenish-blue color of the solution of **15** changed to yellow during electrochemical reduction, and reverse oxidation of the yellow-colored solution regenerated the visible spectra of **15**. The color of the solution of **16** changed from green to yellow during the electrochemical reduction with the decrement of an original absorption band in the visible region. However, reverse oxidation of the yellow solution generated did not regenerate the parent spectrum of **16**, completely.

Recently, we have reported the electrochromic behavior of the thiophene-substituted TCNE-adducts, which show a reversible color change in the electrochemical redox sequence.[13] The reversibility of the color changes might be ascribed to the formation of a stabilized closed-shell dianionic species with thienoquinoid structure in the two-electron reduction. Although the thiophene-substituted TCNQ-adducts **13**, **17** and **18** also exhibited a reversible multistage reduction wave on CV, these adducts did not exhibit reversible color changes in redox sequence under the conditions of the spectral measurements (Fig. 4).

It is well known that the radical anion of DCNQ derivatives readily dimerizes to form σ-bond between the two DCNQ moieties.[18] Thus, the irreversibility of the color changes of DCNQ derivatives **10–18** should be reasoned by the σ-bond formation caused by the coupling of the intermediary forming radical anion exhibiting dimerization and/or polymerization of the DCNQ moiety by the electrochemical reduction.

Conclusions

In conclusion, we have described the synthesis and electronic properties of 2*H*-cyclohepta[*b*]furan-2-one-substituted DCNQs by absorption spectroscopy, theoretical calculation, CV and DPV, and electrochromic analysis.

The novel 2*H*-cyclohepta[*b*]furan-2-one-substituted DCNQs **10–18** were synthesized in a one-step procedure consisting of the formal [2 + 2] cycloaddition reaction of the arylethynyl-2*H*-cyclohepta[*b*]furan-2-ones **1–9** with TCNQ, followed by the ring opening reaction of the initially formed cyclobutene derivatives. Strong ICT absorption bands with large solvent dependence in their UV/Vis spectra featured these 2*H*-cyclohepta[*b*]furan-2-one-substituted DCNQs. Furthermore, their transition state was characterized by TD-DFT calculations. An analysis by CV and DPV revealed that these compounds **10–18** exhibit a reversible multistep reduction wave dependent on the number of DCNQ units in the molecule. In contrast to the results on the TCBD derivatives, DCNQs **10–18** showed poor reversibility of electrochromic behavior, although a significant color change was observed during the electrochemical reduction.

These results could lead to progress of donor–acceptor systems for applications in organic electronics and optoelectronic materials. For the creation of advanced organic materials, preparation of TCBDs and DCNQs with different π-electron systems is now in progress in our laboratory.

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