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Donor−Acceptor Chromophores

Synthesis, Properties and Redox Behavior of 1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadienes Connected by Aryl, Biaryl and Teraryl Spacers

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Abstract: Aryl-substituted 1,1,4,4-tetracyano-1,3-butadienes **11−14** and bis(1,1,4,4-tetracyanobutadiene)s **15−19**, possessing a ferrocenyl group on each terminal, were prepared by the reaction of alkynes **2−10** with tetracyanoethylene (TCNE) in a [2 + 2] cycloaddition reaction, followed by retroelectrocyclization of the initially formed [2 + 2] cycloadducts (i.e., cyclobutene derivatives). The characteristic intramolecular charge-transfer (ICT) between the donor (ferrocene) and acceptor (TCBD) moieties were investigated by UV/Vis spectroscopy. The redox behavior of FcTCBDs **11−14** and bis-FcTCBDs **15−19** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which revealed their properties of multi-electron transfer depending on the number of ferrocene and TCBD moieties. Moreover, significant color changes were observed by visible spectroscopy under the electrochemical reduction conditions.

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Introduction

Ferrocene has attracted the interest due to its facile redox properties, with a rather low oxidation potential that allows it to form a stabilized radical cationic state (ferrocenium ion). A large number of donor–acceptor systems possessing a ferrocenyl-donor group have been synthesized and their properties represented by their characteristic redox properties with an amphoteric redox behavior have been extensively studied.[1]

As an attempt to realize the donor–acceptor systems possessing a ferrocenyl-donor group, [2 + 2] cycloaddition–retroelectrocyclization (CA–RE) of ethynylferrocene derivatives with electron-deficient olefins has been examined.[2] Diederich *et al*. have extensively extended these types of chemistries.[3] A variety of ferrocene-substituted 1,1,4,4-tetracyano-1,3-butadienes (TCBDs), dicyanoquinodimethanes (DCNQs) and bicyclo[4.2.0]octane derivatives, which showed promising nonlinear optical properties, has been prepared by the group from the reaction of ferrocene-substituted alkynes and butadiynes with tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). More recently, Michinobu reported the reaction of ferrocene-containing poly(aryleneethynylene) derivatives with TCNE to give ferrocene-substituted polyTCBDs, which could become promising candidates for the application to organic optoelectronic devices such as nonlinear optics and photovoltaics.[4]

We have also reported the synthesis and electrochemical properties of TCBD[5] and DCNQ[6] derivatives with ferrocenyl functions, which have been prepared by the [2 + 2] CA–RE reaction of the corresponding ethynylferrocene derivatives with TCNE and TCNQ. In the study, we have revealed their multi-step

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reduction properties by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Moreover, significant color changes are also observed by the electrochemical reduction of the new ferrocene-substituted chromophores with the TCBD and DCNQ moieties. However, systematic investigation of the influence of the ferrocenyl function toward the TCBD derivatives has not yet been explored. The optical and electrochemical properties of the TCBD derivatives could strongly be affected by the substituted π-electron groups. An intensive investigation of the effect of π-electron systems connected to the TCBD units with a ferrocenyl function should provide useful information for the creation of the electronic devices utilizing their amphoteric redox properties.

Herein, we describe the Pd-catalyzed synthesis of a series of ethynylferrocene derivatives substituted by several π-electron systems, as well as transformation to the aryl-substituted TCBDs and bis(1,1,4,4-tetracyanobutadiene)s (bis-TCBDs) connected by arylene, biarylene and terarylene spacers, possessing a ferrocenyl group on each terminal by the [2 + 2] CA–RE reaction with TCNE. The electronic properties of the novel ferrocene-substituted TCBD and bis-TCBD derivatives (FcTCBDs and bis-FcTCBDs) substituted by several π-electron systems were investigated by absorption spectroscopy and electrochemical analysis.

Results and Discussion

Synthesis: The synthesis of a series of ethynylferrocene derivatives substituted by several π-electron systems **2−10** has been already reported in the literature.[7−13] Thus, these compounds are prepared by Pd-catalyzed cross-coupling reaction of ethynylferrocene (**1**) with the corresponding iodoarenes under Sonogashira−Hagihara conditions according to the literatures. The yield of the mono-alkynes **2−5** obtained by this research is summarized in Table 1. The yield of bis-alkynes **6−10** is shown in Schemes 1−3, respectively. ^{1}H NMR chemical shifts and the melting point of the products confirmed the formation of the ethynylferrocene derivatives **2−10** shown in the literatures. Moreover, EI mass spectra of the products showed the correct molecular ion peaks as $[M]^+$ ions (see Supporting Information). Thus, these alkyne derivatives were utilized in further transformations for the synthesis of the novel FcTCBD and bis-FcTCBD derivatives.

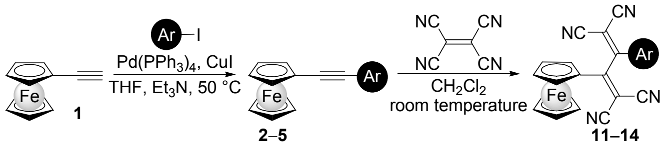
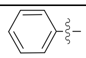
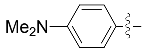
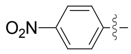
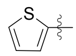
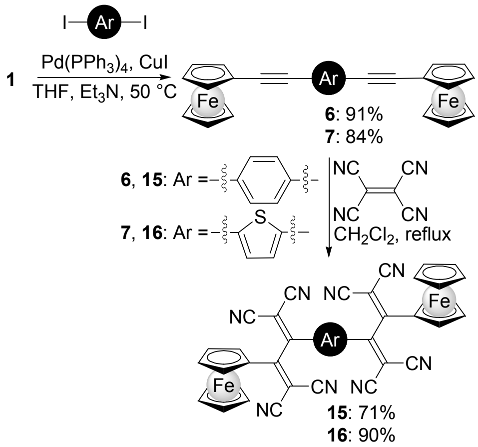


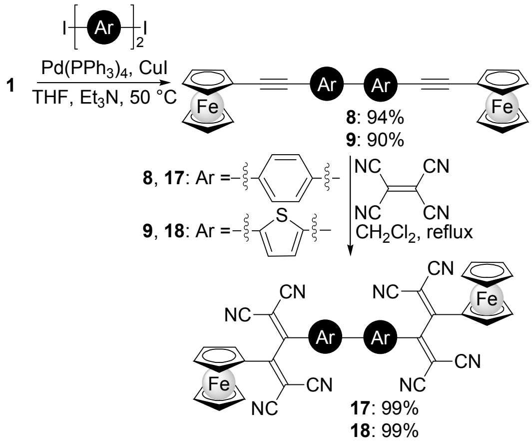
Table 1. Synthesis and reaction of ferrocenylethynylarenes **2−5**.

Ar	Sonogashira reaction Product, Yield [%][a]	[2 + 2] CA–RE reaction Product, Yield [%][a]
	**2**, 61	**11**, 97
	**3**, 98	**12**, 91
	**4**, 72	**13**, 95
	**5**, 99	**14**, 91

[a] Isolated yield.



Scheme 1. Synthesis of bis-FcTCBDs **15** and **16** with an aryl spacer.



Scheme 2. Synthesis of bis-FcTCBDs **17** and **18** with a biaryl spacer.

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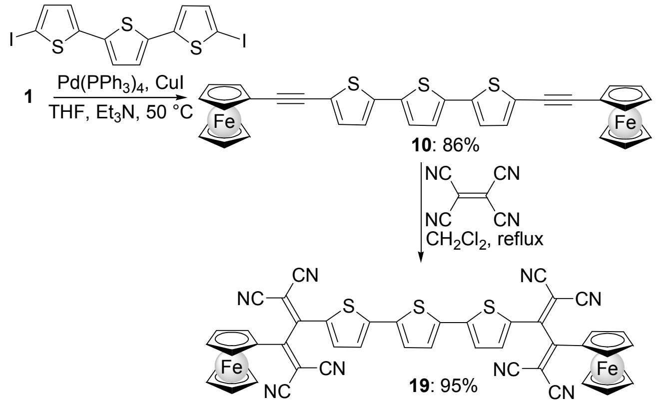


Scheme 3. Synthesis of bis-FcTCBD **19** with a terthiophenediyl spacer.

For the synthesis of the novel FcTCBDs and bis-FcTCBDs, [2 + 2] CA–RE sequence of **2−10** with TCNE was conducted according to the previously described procedure.[2−5] The reaction of **2**[7] with TCNE in CH_2Cl_2 at room temperature yielded **11** in 97% yield as a sole product. The reaction of **3**[8], which has an electron-donating *N,N'*-dimethylamino group at the *p*-position on the benzene ring, with TCNE in CH_2Cl_2 gave **12** in 91% yield. Alkyne derivative **4**[9], which possesses a nitro group at the *p*-position on the benzene ring, also reacted readily with TCNE, as similar to the reactions of **2** and **3**, to afford the corresponding TCBD derivative **13** in 95% yield (Table 1). It is noteworthy that the reaction of **4** readily proceeded under mild conditions, although the electron-withdrawing group, the nitro group, is substituted on the benzene ring. The high reactivity can be attributed to the electron-donating nature of the substituted-ferrocene ring, because highly electron-donating group in the alkyne terminal is required to succeed the [2 + 2] CA–RE reaction with TCNE. Similar to the results on the aryl derivatives, the [2 + 2] CA–RE reaction of the thiophene derivative **5**[9] with TCNE in CH_2Cl_2 at room temperature afforded **14** in 91% yield (Table 1).

The double-addition of TCNE to **6**[10] and **7**[11] gave **15** and **16** in 71% and 90% yields, respectively, by stirring in CH_2Cl_2 at the reflux temperature (Scheme 1). Bis-FcTCBD chromophores, each bearing a biarylene spacer, **17** and **18** were obtained in 99% and 99% yields, respectively, by the [2 + 2] CA–RE reaction of bis(ethynylferrocene) precursors **8**[12] and **9**[12] with TCNE (Scheme 2). Bis-FcTCBD **19** connected with terthiophenediyl spacer was also obtained in excellent yield (95%) by the [2 + 2] CA–RE reaction of the corresponding bisalkyne **10**[13] with TCNE (Scheme 3). The new FcTCBD and bis-FcTCBD chromophores **11−19** are stable, deeply colored crystals that can be stored in the crystalline state at ambient temperature under aerobic conditions.

Spectroscopic Properties: The novel FcTCBDs and bis-FcTCBDs **11−19** were fully characterized on the basis of their spectral data, as summarized in the Experimental Section. The NMR assignment of the reported compounds was confirmed by COSY, HMQC and HMBC experiments. High-resolution mass spectra of **11−19** ionized by FAB and ESI showed the correct molecular ion peaks. The characteristic stretching vibration band of the C≡N moiety of the FcTCBDs **11−14** and bis-FcTCBDs **15−19** was observed at ν_{max} = 2219−2224 cm^{-1} in their IR spectra. These results are consistent with the given structure of these products.

UV/Vis spectra of FcTCBDs **11–13** with an aryl substituent, and FcTCBD **14** and bis-FcTCBDs **16**, **18** and **19** with a 2-thienyl substituent and 2,5-thiophenediyl spacers are shown in Figures 1 and 3. FcTCBDs **11** and **13** exhibited a broad CT absorption centered at λ_{max} = 621 nm and λ_{max} = 627 nm, respectively, which spread up to 850 nm (Figure 1). Previously, Mochida *et al*. reported that 2,5-dicyano-3-ferrocenylhexa-2,4-dienedinitrile (**20**) exhibits a broad absorption centered at λ_{max} = 632 nm in CH_2Cl_2 (Figure 2),[4] which was explained by an ICT arising from the π–π* transition from ferrocene to TCBD moieties. Therefore, the longest wavelength absorption of compound **11** and **13** could be ascribed to the ICT absorption from ferrocene to the TCBD units. On the other hand, UV/Vis spectra of the FcTCBD **12** with *N,N'*-dimethylanilino substituent exhibited a strong absorption band at λ_{max} = 469 nm. The absorption band of **12** should be concluded to the ICT from *N,N'*-dimethylanilino group to FcTCBD unit, since the wavelength of the absorption maximum of **12** resembled with that of TCBD **21** (λ_{max} = 481 nm)[14] with *N,N'*-dimethylanilino substituent. The broad ICT absorption The FcTCBD **12** also exhibited a broad ICT absorption band at around 600 nm, similar with FcTCBDs **11** and **13**. FcTCBD **14** with a 2-thienyl substituent showed a broad absorption band at λ_{max} = 627 nm, that should correspond to that of FcTCBDs **11**−**13**, arising from the ICT from ferrocene to the TCBD unit.

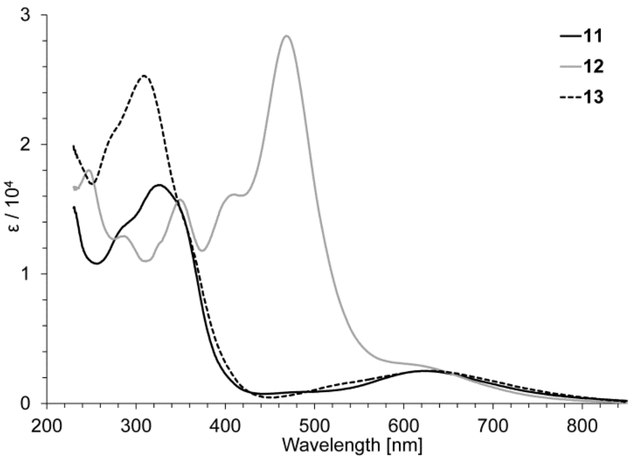
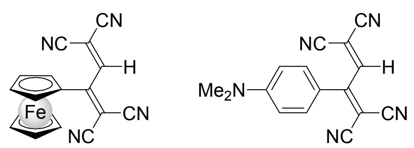


Figure 1. UV/Vis spectra of **11** (black line), **12** (gray line) and **13** (broken line) in CH_2Cl_2.



20 **21**

Figure 2. FcTCBD **20** and TCBD **21** with a ferrocenyl and an *N,N'*-dimethylanilino substituent.

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UV/Vis spectra of bis-FcTCBDs **15** and **17** connected by 1,4-phenylene and 4,4'-biphenylene spacers revealed a broad absorption band at λ_{max} = 616 nm in DMSO[15] and λ_{max} = 626 nm in CH_2Cl_2, respectively, which reached to near infrared region. In contrast, absorption maxima of **18** (λ_{max} = 476 nm) and **19** (λ_{max} = 532 nm) exhibited a bathochromic shift relative to that of **16** (λ_{max} = 437 nm), resulting from the extension of the π-electron system by bi- and terthiophene units. Absorption coefficients of the ICT absorption bands of bis-FcTCBDs **16** (log ε 4.37), **18** (log ε 4.72) and **19** (log ε 4.83), probably due to the transition from the thiophenediyl, bithiophenediyl and terthiophenediyl spacers to FcTCBD unit, largely increased in this order compared with that of thiophene-substituted FcTCBD **14** as shown in Figure 3. Absorption coefficient for the longest wavelength band of **16** was almost twice as large as that of **14**, due to the overlap of the two ICT from ferrocene to the TCBD unit. Thus, the ICT from ferrocene to the TCBD unit in **18** and **19** may be observed as an overlap of the ICT from the spacers to the FcTCBD unit.

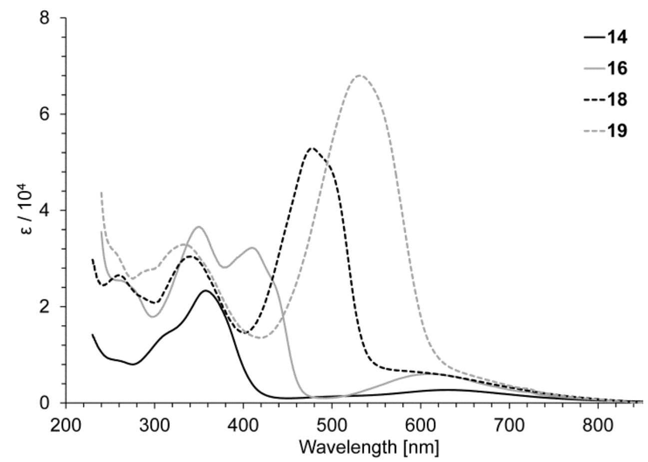


Figure 3. UV/Vis spectra of **14** (black line), **16** (gray line), **18** (black-broken line) and **19** (gray-broken line) in CH_2Cl_2.

Electrochemistry: To clarify the effect on the electrochemical properties of aromatic substituents on the FcTCBD derivatives and spacer groups on the bis-FcTCBD derivatives, the redox behavior of the novel chromophores **11−19** 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 a platinum wire auxiliary and disk working electrodes. All measurements were carried out under an argon atmosphere, and the potentials were related to a standard $Ag/AgNO_3$ reference electrode. The half-wave potential of the ferrocene−ferrocenium ion couple (Fc/Fc^+) under these conditions using this reference electrode was observed at +0.15 V on CV. Accuracy of the reference electrode was confirmed by CV measurements of the couple in each sample as an internal ferrocene standard. The redox potentials (in volts vs $Ag/AgNO_3$) of **11−19** measured under a scan rate of 100 mVs^{-1} are summarized in Table 2.

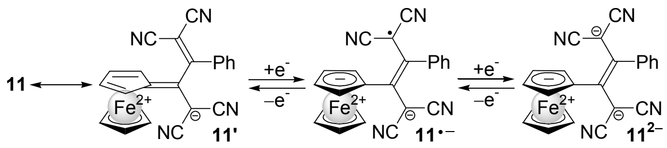
Table 2. Redox potentials[a,b] of the FcTCBD derivatives **11−14** and **20** and the bis-FcTCBD derivatives **15−19**.

Sample	Method	E_1^{ox} [V]	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]
11	CV	+0.59	−0.78	−1.10	
	(DPV)	(+0.57)	(−0.76)	(−1.08)	
12	CV	+0.55	−0.95	−1.20	
	(DPV)	(+0.53)	(−0.93)	(−1.18)	
13	CV	+0.61	−0.64	−0.97	
	(DPV)	(+0.59)	(−0.62)	(−0.95)	
14	CV	+0.60	−0.78	−1.05	
	(DPV)	(+0.58)	(−0.76)	(−1.03)	
15	CV	+0.61	−0.60	−0.75	−1.18
	(DPV)	(+0.59)	(−0.58)	(−0.73)	(−1.16)
16	CV	+0.59	−0.39	−0.66	−1.27
	(DPV)	(+0.57)	(−0.37)	(−0.64)	(−1.25)
17	CV	+0.59	−0.75	−1.08	
	(DPV)	(+0.57)	(−0.73)	(−1.06)	
18	CV	+0.60	−0.63	−0.73	−1.11
	(DPV)	(+0.58)	(−0.61)	(−0.71)	(−1.09)
19	CV	+0.58	−0.73	−0.75	−1.04
	(DPV)	(+0.56)	(−0.71)	(−0.73)	(−1.02)
20[5c]	CV	+0.58	−0.60		
	(DPV)	(+0.56)	(−0.58)	(−0.98)	

[a] V vs. $Ag/AgNO_3$, 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). [b] Half-wave potentials E^{ox} and E^{red} = (E_{pc} + E_{pa})/2 on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

All of the FcTCBD and bis-FcTCBD chromophores **11−19** showed a reversible one-stage oxidation and a two- or three-stage reduction wave on CV, due to the oxidation of the ferrocene moieties and the reduction of the TCBD units, respectively. Plausible redox behavior of FcTCBD **11** under the electrochemical reduction conditions is illustrated in Scheme 4. The first oxidation potential of FcTCBDs **11−14** and bis-FcTCBDs **15−19** was observed at a similar potential region (+0.55 V to +0.61 V) on CV under the electrochemical oxidation, which resembles to that of much simpler FcTCBD **20** (+0.58 V).[5c] Thus, it should be concluded that the aromatic substituent effect on the FcTCBD unit in compounds **11−14** and the interaction between the two ferrocene units in the bis-FcTCBDs **15−19** through the aromatic spacers are relatively low, from the view point of their oxidation potentials.

Meanwhile, the reduction potentials were significantly affected by the aromatic substituents on the FcTCBDs **11−14** and aromatic spacers in the bis-FcTCBDs **15−19**. FcTCBD chromophores **11−13** with an aromatic substituent displayed a reversible two-stage reduction wave, which should be attributed to the stepwise reduction to a radical anionic and a dianionic species. The first reduction potential was depended on the nature of the *p*-substituent on the aromatic ring, that is, the first reduction potential of **13** (−0.64 V) was less negative than those of **11** (−0.78 V) and **12** (−0.95 V). These results reflect that the electron-withdrawing nitro substituent on the aromatic ring directly affects to decrease the LUMO level of the molecule. Electrochemical reduction of FcTCBD with thiophene moiety **14** also showed a reversible two-step reduction wave at half-wave potentials of −0.78 V and −1.05 V on CV, which should also be attributed to the stepwise formation of a radical anionic and a dianionic species, respectively.



Scheme 4. Plausible redox behavior of **11** under the electrochemical reduction conditions.

Electrochemical reduction of bis-FcTCBDs **15**−**19** showed a reversible two or three-stage wave by CV depending on the spacer groups, which could be attributed to the formation of anionic secies up to the tetraanions. Bis-FcTCBDs **15** (−0.60 V, −0.75 V and −1.18 V) and **16** (−0.39 V, −0.66 V and −1.27 V) exhibited a reversible three-step reduction wave, in which the third reduction wave was a two-electron transfer in one step to form a tetraanionic species. Although the bis-FcTCBDs **15** and **16** have a symmetrical structure, two TCBD units showed a stepwise reduction by CV. This means the existence of redox interaction between the intramolecular two FcTCBD moieties through the 1,4-phenylene and 2,5-thiophenediyl spacers. Moreover, the first reduction potentials of bis-FcTCBDs **15** and **16** decreased definitely compared with that of the corresponding FcTCBDs **11** and **14**. This indicates that the connection of the two FcTCBD units by the spacers reduces the LUMO level and increases the electron-affinity of the molecules, owing to the effective π-conjugation through the aromatic spacers. As shown in Table 2, bis-FcTCBDs **17**−**19** with biarylene and terthiophenediyl spacers also showed a reversible multi-electron reduction wave on CV. The first reduction potential of bis-FcTCBDs **17**−**19** became much closer to that of the corresponding FcTCBDs **11** and **14**, according to the extension of the arylene spacer. These results support the idea that the extension of π-electron systems between the FcTCBD units decreases an electronic interaction among the FcTCBD units in the molecules, due to the less effective conjugation between the two FcTCBD units through the aromatic spacers.

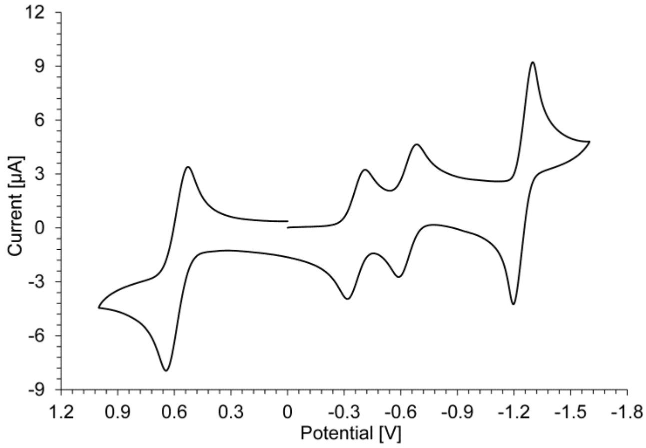


Figure 4. Cyclic voltammogram of the reduction of **16** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1}.

A violene−cyanine hybrid was proposed by Hünig *et al*. for the design of a stabilized organic electrochromic systems.[16] We have also reported a more general structural principle through the combination of violene and cyanine-type substructures with a large variability.[17] We have identified some novel hybrid structures of violenes and cyanines during the study on the synthesis and redox behavior of TCBDs and DCNQs substituted by ferrocene,[5,6] azulene[18] and 2*H*-cyclohepta[*b*]furan-2-one[19] moieties, in addition to the Hünig's violene−cyanine hybrid structure. Similar to the TCBDs and DCNQs derivatives reported by us previously, novel FcTCBDs **11**−**14** and bis-FcTCBDs **15**−**19** might become new examples of the redox systems for the extensions of the hybrid structures of violenes and cyanines with multi-electron transfer. Thus, the visible spectra of **11**−**19** were monitored to clarify the color changes observed during the electrochemical reactions.

Constant-current oxidation and reduction (100 μA) was applied to solutions of **11**−**19** with a platinum mesh as the working electrode and a wire counter electrode in an electrolytic cell of 1 mm thickness. Visible spectra were measured in degassed benzonitrile containing Et_4NClO_4 (0.1 M) as supporting electrolyte at room temperature under the electrochemical reaction conditions.[20] We expected the reversible color change of the solutions under the electrochemical oxidation conditions owing to the generation of a stabilized ferrocenium ion. However, reversibility was not observed in the electrochromic study on **11**−**19** under the conditions of the spectral measurements. These results might be concluded that the generated ferrocenium ion is destabilized by the strong electron-withdrawing TCBD moieties under the measurement conditions. In contrast, reversible color change of the solution of **11**, **13** and **14** from blue to yellow was observed during the electrochemical reduction, although compound **12** did not show any color changes under the conditions. Reversibility of the yellow-colored solution was observed as reflected by good reversibility of CV.

Similarly, the blue color of the solution of bis-FcTCBD **15** changed to yellow during the electrochemical reduction, and the yellow-colored solution regenerated the visible spectrum of **15** by the reverse oxidation. When the UV/Vis spectrum of bis-FcTCBD **16** was measured under the electrochemical reduction conditions, new absorption bands in the visible region at λ_{max} = 600 nm and λ_{max} = 725 nm, which spread into the near-infrared region, gradually developed (Figure 4). The reverse oxidation decreased the new absorption bands, and regenerated the original absorption bands of **16**.

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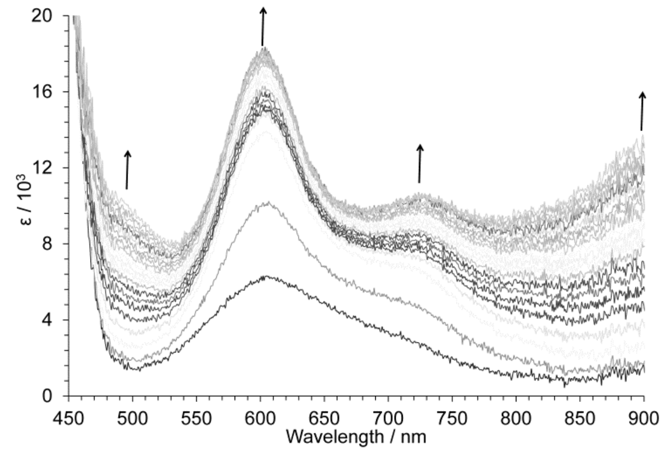

Figure 5. Continuous change in the UV/Vis spectrum of **16** under constant-current electrochemical reduction (100 μA) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

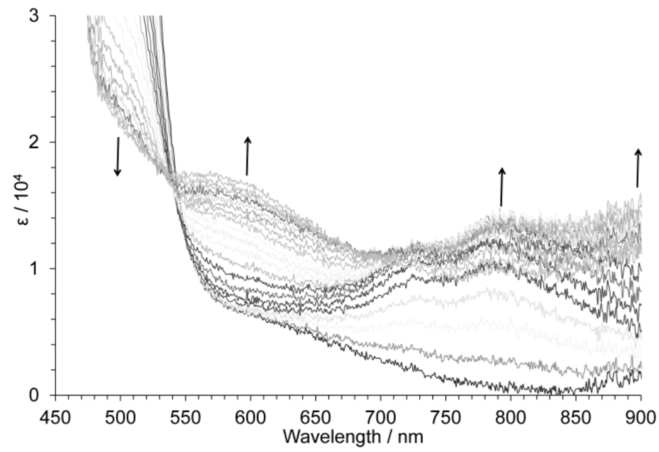

Figure 6. Continuous change in the UV/Vis spectrum of **18** under constant-current electrochemical reduction (100 μA) in benzonitrile containing Et_4NClO_4 (0.1 M) at 20 sec intervals.

Visible spectra of bis-FcTCBD **17** with biphenylene spacer were also measured under electrochemical reduction conditions. The absorption band in the near-infrared region gradually developed along with a color change from blue to red. Reverse oxidation of the reduced species regenerated the original color of **17**. Reversible color change from red to blue was also observed in bis-FcTCBD **18** with bithiophenediyl spacer. The absorption band in the visible region of **18** gradually increased with the development of new absorption bands in the near-infrared region along with an isosbestic point during the electrochemical reduction. Reverse oxidation of the reduced species decreased the new absorption bands, along with recovery of the original spectrum of **18**. The absorption bands of **19** in the visible region also gradually disappeared during the electrochemical reduction. However, reverse oxidation of the reduced species regenerated the absorption of **19**, incompletely. It is noteworthy that the bis-FcTCBD **19** did not exhibit a reversible color change. Whereas, FcTCBD derivatives connected by 2,5-thiophenediyl and 2,5'-bithiophenedily spacers **16** and **18** showed a reversible color change and development of new absorption bands spread up to the near-infrared region. These results indicate the formation of a destabilized closed-shell dianionic species with a thienoquinoid structure from the two-electron reduction of **19**, contrary to the reversible color change of FcTCBD derivatives connected by 2,5-thiophenediyl and 2,5'-bithiophenedily spacers **16** and **18**.

Conclusion

A series of ethynylferrocenes **2−10** substituted by several π-electron systems were prepared by palladium-catalyzed Sonogashira–Hagihara reaction. Aryl-substituted TCBDs **11−14** and bis-TCBDs **15−19** connected by arylene, biarylene and terarylene spacers, possessing a ferrocenyl group on each terminal, were synthesized in a one-step procedure consisting of formal [2 + 2] cycloaddition reaction of **2−10** with TCNE, followed by retroelectrocyclization of the initially formed cyclobutene derivatives. Intramolecular CT absorption bands were found in UV/Vis spectra of the FcTCBD and bis-FcTCBD chromophores **11−19**. Analyses by CV and DPV showed that the TCBDs and bis-FcTCBDs **11−19** exhibited a reversible multi-stage reduction wave, as well as a reversible one-stage oxidation wave. Moreover, significant color changes were observed during the electrochemical reduction. In particular, bis-FcTCBDs **16** and **18** constructed by thiophenediyl and bithiophenediyl spacers exhibited significant color changes with high reversibility, attributable to the stabilization of di- and tetraanionic species during the electrochemical reaction. These results showed that FcTCBDs and bis-FcTCBDs behave like a violene−cyanine hybrid, a concept proposed by Hünig and co-workers, in view of the formation of the stabilized closed-shell di- and tetraanionic species by the two- or four electron reduction.

To evaluate the scope of this class of molecules investigated by this research, the preparation of novel TCBD chromophores connected with various π-electron cores is now in progress in our laboratory.

Experimental Section

General: Melting points were determined with a Yanagimoto MPS3 micro melting apparatus and are uncorrected. High resolution mass spectra were obtained with a Bruker Daltonics APEX III instrument. IR and UV−Vis spectra were measured with JASCO FT/IR-4100 and Shimadzu UV-2550 spectrophotometer. 1H and 13C NMR spectra were recorded with a JEOL ECA500 at 500 MHz and 125 MHz, respectively. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from Ag/AgNO3 (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M). Elemental analyses were measured with Thermo FlashEA1112 or performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

1,1,4,4-Tetracyano-2-ferrocenyl-3-phenyl-1,3-butadiene (11): To a solution of **2** (100 mg, 0.35 mmol) in CH_2Cl_2 (10 mL) was added TCNE (64 mg, 0.50 mmol). The resulting mixture was stirred at room temperature for 1 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **11** (140 mg, 97%) as blue crystals. M.p. > 300 °C (CH_2Cl_2/hexane); IR (KBr disk): ν_{max} = 2957 (w), 2927 (w), 2224 (m, C≡N), 1561 (w), 1507 (s), 1489 (m), 1449 (m), 1404 (w), 1382 (w), 1338 (w), 1291 (w), 1264 (w), 1185 (w), 1157 (w), 1110 (w), 1053 (w), 1042 (w), 1003 (w), 939 (w), 822 (m), 784 (w), 765 (m), 700 (m), 671 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 284 sh (4.13), 327 (4.23), 472 sh (2.94), 621 (3.40) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.63−7.60 (m, 3H, *o,p*-Ph), 7.53 (dd, 2H, *J* = 7.5, 1.0 Hz, *m*-Ph), 5.29 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 4.98 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.85 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.63 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 4.38 (s, 5H, Cp) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 172.3 (*C*=C(CN)$_2$), 166.6 (*C*=C(CN)$_2$), 134.1 (*p*-Ph), 131.3 (*ipso*-Ph), 129.8 (*o*-Ph), 128.5 (*m*-Ph), 113.6 (CN), 112.9 (CN), 111.5 (2×CN), 86.5 (*C*(CN)$_2$), 78.4 (*C*(CN)$_2$), 75.9 (Fc), 75.1 (Fc), 74.6 (Fc), 72.6 (Cp), 72.5 (Fc), 71.3 (Fc) ppm. HR−FAB−MS (positive): calcd for $C_{24}H_{14}N_4Fe$ [M$^+$], 414.0568; found: 414.0588. Anal. Calcd for $C_{24}H_{14}N_4Fe$: C, 69.59; H, 3.41; N, 13.53. Found: C, 69.35; H, 3.44; N, 13.47.

p-(1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadien-3-yl)-N,N'-dimethylaniline (12): To a solution of **3** (100 mg, 0.30 mmol) in CH_2Cl_2 (10 mL) was added TCNE (58 mg, 0.45 mmol). The resulting mixture was stirred at room temperature for 2 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **12** (125 mg, 91%) as reddish brown crystals. M.p. 204–205 °C (CH_2Cl_2/hexane); IR (KBr disk): ν_{max} = 2925 (w), 2219 (m, C≡N), 1603 (s), 1503 (s), 1438 (m), 1382 (s), 1341 (m), 1321 (m), 1281 (m), 1207 (m), 1180 (m), 1106 (w), 1052 (w), 1001 (w), 941 (w), 904 (w), 827 (m), 812 (m), 783 (w), 743 (w), 700 (w), 655 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 247 (4.26), 284 (4.11), 324 sh (4.08), 349 (4.20), 411 (4.21), 469 (4.45), 626 sh (3.45) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.67 (d, 2H, *J* = 9.5 Hz, *o*-Ph), 6.65 (d, 2H, *J* = 9.5 Hz, *m*-Ph), 5.22 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 4.91 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.80 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.67 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 4.44 (s, 5H, Cp), 3.12 (s, 6H, NMe$_2$) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 174.6 (*C*=C(CN)$_2$), 163.1 (*C*=C(CN)$_2$), 154.0 (*p*-Ph), 132.0 (*o*-Ph), 117.5 (*ipso*-Ph), 114.3 (CN), 113.9 (CN), 113.7 (CN), 112.8 (CN), 111.76 (*m*-Ph), 79.3 (*C*(CN)2), 76.2 (*C*(CN)$_2$), 75.0 (Fc), 74.5 (Fc), 74.2 (Fc), 72.3 (Cp), 71.9 (Fc), 71.8 (Fc), 40.1 (NMe$_2$) ppm. HR−FAB−MS (positive): calcd for $C_{26}H_{19}FeN_5^+$ [M$^+$], 457.0990; found: 457.0972. Anal. Calcd for $C_{26}H_{19}FeN_5$: C, 68.29; H, 4.19; N, 15.31. Found: C, 68.20; H, 4.25; N, 15.26.

***p*-(1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadien-3-yl)nitrobenzene (13):** To a solution of **4** (104 mg, 0.31 mmol) in CH_2Cl_2 (5 mL) was added TCNE (62 mg, 0.48 mmol). The resulting mixture was stirred at room temperature for 24 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **13** (135 mg, 95%) as a blue oil. IR (KBr disk): ν_{max} = 3106 (w), 2858 (w), 2222 (m, C≡N), 1602 (w), 1525 (s), 1442 (m), 1409 (w), 1381 (w), 1351 (s), 1291 (w), 1263 (w), 1187 (w), 1108 (w), 1047 (w), 1006 (w), 937 (w), 904 (w), 846 (m), 777 (w), 747 (w), 696 (w), 657 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 272 sh (4.31), 308 (4.40), 360 sh (4.11), 525 sh (3.16), 627 (3.40) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.34 (d, 2H, *J* = 9.0 Hz, *m*-Ph), 7.72 (d, 2H, *J* = 9.0 Hz, *o*-Ph), 5.52 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 5.08 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.90 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.47 (s, 5H, Cp), 4.42 (br s, 1H, Fc) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 171.1 (*C*=C(CN)$_2$), 164.0 (*C*=C(CN)$_2$), 150.2 (*p*-Ph), 136.6 (*ipso*-Ph), 129.7 (*o*-Ph), 124.8 (*m*-Ph), 113.3 (CN), 112.8 (CN), 110.8 (CN), 110.6 (CN), 89.5 (*C*(CN)$_2$), 78.7 (*C*(CN)$_2$), 76.6 (Fc), 75.4 (Fc), 74.1 (Fc), 73.0 (Cp), 70.9 (Fc) ppm, One signal of Fc is overlapped with other signal. HR−FAB−MS (positive): calcd for $C_{24}H_{13}N_5O_2Fe^+$ [M+], 459.0419; found: 459.0401. Anal. Calcd for $C_{24}H_{13}N_5O_2Fe$: C, 62.77; H, 2.85; N, 15.25. Found: C, 62.61; H, 2.93; N, 15.18.

2-(1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadien-3-yl)thiophene (14): To a solution of **5** (100 mg, 0.34 mmol) in CH_2Cl_2 (10 mL) was added TCNE (65 mg, 0.51 mmol). The resulting mixture was stirred at room temperature for 3 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **14** (130 mg, 91%) as a blue oil. IR (KBr disk): ν_{max} = 3106 (w), 2223 (m, C≡N), 1526 (s), 1442 (m), 1407 (s), 1367 (m), 1347 (m), 1270 (w), 1237 (w), 1107 (w), 1061 (w), 1003 (w), 935 (w), 829 (m), 733 (s), 705 (w), 665 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 309 sh (4.14), 358 (4.37), 498 sh (3.12), 627 (3.43) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.29 (dd, 1H, *J* = 4.0, 1.0 Hz, 3-H of Th), 7.20 (dd, 1H, *J* = 4.0, 1.0 Hz, 5-H of Th), 6.76 (dd, 1H, *J* = 4.0, 4.0 Hz, 4-H of Th), 5.38 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 5.02 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.88 (ddd, 1H, *J* = 1.5, 1.5, 1.5 Hz, Fc), 4.62 (dd, 1H, *J* = 1.5, 1.5 Hz, Fc), 4.59 (s, 5H, Cp) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 172.2 (*C*=C(CN)$_2$), 156.9 (*C*=C(CN)$_2$), 137.5 (C-3 of Th), 136.8 (C-5 of Th), 134.3 (C-2 of Th), 129.6 (C-4 of Th), 113.5 (CN), 112.5 (2×CN), 112.1 (CN), 79.2 (*C*(CN)$_2$), 79.0 (*C*(CN)$_2$), 75.9 (Fc), 75.6 (Fc), 74.9 (Fc), 72.7 (Cp), 72.3 (Fc), 71.6 (Fc) ppm. HR−FAB−MS (positive): calcd for $C_{22}H_{12}FeN_4S^+$ [M$^+$], 420.0132; found: 420.0133. Anal. Calcd for $C_{22}H_{12}FeN_4S$: C, 62.87; H, 2.88; N, 13.33. Found: C, 62.70; H, 2.95; N, 13.30.

1,4-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)benzene (15): To a solution of **6** (134 mg, 0.27 mmol) in CH_2Cl_2 (8 mL) was added TCNE (103 mg, 0.80 mmol). The resulting mixture was refluxed for 3 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **15** (144 mg, 71%) as green crystals. M.p. 250 °C decomp. (MeCN); IR (KBr disk): ν_{max} = 3098 (w), 2220 (m, C≡N), 1558 (m), 1518 (s), 1442 (m), 1413 (w), 1384 (w), 1332 (w), 1260 (w), 1188 (w), 1105 (w), 1066 (w), 1016 (w), 940 (w), 899 (w), 843 (m), 808 (w), 756 (w), 710 (w), 665 (m) cm^{-1}; UV/Vis (DMSO): λ_{max} (log ε) = 255 (4.59), 353 (4.47), 474 (4.60), 616 (3.65) nm; ^{1}H NMR (500 MHz, acetone-d$_6$): δ_H = 8.23 (s, 2H, Ph), 8.22 (s, 2H, Ph), 5.31 (m, 1H, Fc), 5.29 (m, 1H, Fc), 5.05 (m, 4H, Fc), 4.97 (m, 1H, Fc), 4.93 (m, 1H, Fc), 4.32 (s, 5H, Cp), 4.30 (s, 5H, Cp) ppm. Low solubility hampered the measurement of ^{13}C NMR. HR−ESI−MS (positive): calcd for $C_{42}H_{22}Fe_2N_8$ + Na$^+$ [M + Na$^+$], 773.0558; found: 773.0558. Anal. Calcd for $C_{42}H_{22}Fe_2N_8 \cdot H_2O$: C, 65.65; H, 3.15; N, 14.58. Found: C, 65.60; H, 3.19; N, 14.56.

2,5-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)thiophene (16): To a solution of **7** (100 mg, 0.20 mmol) in CH_2Cl_2 (8 mL) was added TCNE (79 mg, 0.62 mmol). The resulting mixture was refluxed for 2 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **16** (136 mg, 90 %) as green crystals. M.p. 260 °C decomp. (CH_2Cl_2/hexane); IR (KBr disk): ν_{max} = 3110 (w), 2219 (m, C≡N), 1536 (s), 1513 (s), 1446 (m), 1412 (w), 1384 (w), 1339 (w), 1310 (w), 1269 (m), 1216 (w), 1174 (w), 1108 (w), 1087 (w), 1051 (w), 1004 (w), 938 (w), 843 (m), 816 (m), 805 (m), 762 (w), 737 (w), 667 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 262 (4.41), 350 (4.56), 410 (4.51), 437 (4.38), 611 (3.78) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.71 (s, 1H, 3,4-H of Th), 7.55 (s, 1H, 3,4-H of Th), 5.59 (br s, 2H, Fc), 5.13 (br s, 2H, Fc), 4.94 (br s, 2H, Fc), 4.50 (s, 5H, Cp), 4.49 (s, 5H, Cp), 4.36 (br s, 2H, Fc) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 170.6 (*C*=C(CN)$_2$), 170.4 (*C*=C(CN)$_2$), 154.64 (*C*=C(CN)$_2$), 154.57 (*C*=C(CN)$_2$), 141.4 (C-2,5 of Th), 141.2 (C-2,5 of Th), 135.8 (C-3,4 of Th), 135.7 (C-3,4 of Th), 113.22 (CN), 113.20 (CN), 112.5 (CN), 112.4 (CN), 111.5 (CN), 111.45 (CN), 111.42 (CN), 111.1 (CN), 84.3 (*C*(CN)$_2$), 84.1 (*C*(CN)$_2$), 78.9 (2×*C*(CN)$_2$), 75.8 (Fc), 75.7 (Fc), 75.02 (Fc), 74.97 (Fc), 73.2 (Cp), 73.0 (Fc), 72.9 (Fc), 71.5 (Fc) ppm; HR−FAB−MS (positive): calcd for $C_{40}H_{20}N_8SFe_2^+$ [M$^+$], 756.0230; found: 756.0215. Anal. Calcd for $C_{40}H_{20}N_8SFe_2$: C, 63.52; H, 2.67; N, 14.81. Found: C, 63.40; H, 2.77; N, 14.76.

1,1'-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)-4,4'-biphenyl (17): To a solution of **8** (136 mg, 0.23 mmol) in CH_2Cl_2 (6 mL) was added TCNE (77 mg, 0.60 mmol). The resulting mixture was refluxed for 2 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **17** (188 mg, 99%) as dark green crystals. M.p. > 300 °C (CH_2Cl_2/hexane); IR (KBr disk): ν_{max} = 3096 (w), 2222 (m, C≡N), 1518 (s), 1423 (s), 1382 (w), 1338 (w), 1314 (m), 1291 (w), 1272 (w), 1178 (w), 1106 (w), 1073 (w), 1001 (w), 936 (w), 835 (m), 803 (m), 751 (w), 735 (w), 665 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 315 sh (4.51), 360 (4.70), 500 sh (3.36), 626 (3.65) nm; ^{1}H NMR (500 MHz, acetone-d$_6$): δ_H = 8.10 (d, 4H, *J* = 8.0 Hz, *o*-Ph), 8.05 (d, 4H, *J* = 8.0 Hz, *m*-Ph), 5.36 (m, 2H, Fc), 5.07 (m, 2H, Fc), 5.01 (br s, 2H, Fc), 4.96 (m, 2H, Fc), 4.36 (s, 10H, Cp) ppm; ^{13}C NMR (125 MHz, acetone-d$_6$): δ_C = 171.7 (*C*=C(CN)$_2$), 165.4 (*C*=C(CN)$_2$), 144.1 (*ipso*-Ph), 132.2 (*p*-Ph), 130.0 (*o*-

Ph), 128.5 (*m*-Ph), 114.1 (CN), 113.9 (CN), 112.24 (CN), 112.21 (CN), 87.7 (*C*(CN)$_2$), 78.7 (*C*(CN)$_2$), 76.1 (Fc), 75.4 (Fc), 74.7 (Fc), 73.3 (Fc), 72.4 (Cp), 71.2 (Fc) ppm. HR−FAB−MS (positive): calcd for $C_{48}H_{26}N_8Fe_2^+$ [M$^+$], 826.0979; found: 826.0981. Anal. Calcd for $C_{48}H_{26}N_8Fe_2$: C, 69.76; H, 3.17; N, 13.56. Found: C, 69.65; H, 3.25; N, 13.51.

2,2'-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)-5,5'-bithiophene (18): To a solution of **9** (100 mg, 0.17 mmol) in CH_2Cl_2 (6 mL) was added TCNE (65 mg, 0.51 mmol). The resulting mixture was refluxed for 2 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **18** (141 mg, 99 %) as purple crystals. M.p. > 300 °C (CH_2Cl_2/hexane); IR (KBr disk): ν_{max} = 3094 (w), 2221 (m, C≡N), 1518 (s), 1424 (s), 1382 (w), 1336 (w), 1314 (w), 1291 (w), 1272 (w), 1182 (w), 1105 (w), 1070 (w), 1004 (w), 935 (w), 897 (w), 833 (m), 752 (w), 692 (w), 665 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 251 (4.41), 337 (4.48), 476 (4.72), 496 sh (4.69), 620 sh (3.78) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.67 (dd, 2H, *J* = 4.0, 4.0 Hz, 3-H of Th), 7.35 (br s, 2H, 4-H of Th), 5.54 (br s, 2H, Fc), 5.06 (br s, 2H, Fc), 4.87 (br s, 2H, Fc), 4.50 (s, 10H, Cp), 4.48 (br s, 2H, Fc) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 171.4 (*C*=C(CN)$_2$), 155.5 (*C*=C(CN)$_2$), 145.0 (C-2 of Th), 137.6 (C-3 of Th), 137.5 (C-3 of Th), 135.6 (C-5 of Th), 128.21 (C-4 of Th), 128.16 (C-4 of Th), 113.5 (CN), 112.5 (CN), 112.4 (CN), 111.9 (CN), 80.3 (*C*(CN)$_2$), 79.5 (*C*(CN)$_2$), 76.2 (Fc), 75.7 (Fc), 75.2 (Fc), 72.9 (Cp), 72.5 (Fc), 71.6 (Fc) ppm. HR−FAB−MS (positive): calcd for $C_{44}H_{22}Fe_2N_8S_2^+$ [M$^+$], 838.0108; found: 838.0082. Anal. Calcd for $C_{44}H_{22}Fe_2N_8S_2{\cdot}H_2O$: C, 61.70; H, 2.82; N, 13.08. Found: C, 61.62; H, 2.85; N 13.06.

2,2''-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)-5,2':5',5''-terthiophene (19): To a solution of **10** (332 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was added TCNE (192 mg, 1.50 mmol). The resulting mixture was refluxed for 3 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 /EtOAc (20:1) to give **19** (437 mg, 95%) as purple crystals. M.p. 172–175 °C (CH_2Cl_2/hexane); IR (KBr disk): ν_{max} = 3100 (w), 2950 (w), 2221 (m, C≡N), 1515 (m), 1413 (s), 1378 (w), 1279 (w), 1224 (w), 1198 (w), 1161 (w), 1097 (w), 1065 (w), 1003 (w), 935 (w), 823 (m), 797 (m), 753 (w), 665 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 256 sh (4.49), 285 sh (4.43), 332 (4.52), 532 (4.83) nm; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 7.61 (dd, 2H, *J* = 4.5, 1.5 Hz, 3-H of Th), 7.35 (s, 2H, 3',4'-H of Th), 7.24 (d, 2H, *J* = 4.5 Hz, 4-H of Th), 5.55 (dd, 2H, *J* = 1.5, 1.5 Hz, Fc), 5.06 (dd, 2H, *J* = 1.5, 1.5 Hz, Fc), 4.87 (dd, 2H, *J* = 1.5, 1.5 Hz, Fc), 4.51 (dd, 2H, *J* = 1.5, 1.5 Hz, Fc), 4.50 (s, 10H, Cp) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 171.9 (*C*=C(CN)$_2$), 155.3 (*C*=C(CN)$_2$), 147.7 (C-2 of Th), 138.5 (C-3 of Th), 137.1 (C-2',5' of Th), 132.9 (C-5 of Th), 128.8 (C-3',4' of Th), 126.1 (C-4 of Th), 113.5 (CN), 112.9 (CN), 112.6 (CN), 112.4 (CN), 78.9 (*C*(CN)$_2$), 77.3 (*C*(CN)$_2$), 76.1 (Fc), 75.6 (Fc), 75.1 (Fc), 72.7 (Cp), 72.4 (Fc), 71.6 (Fc) ppm. HR−FAB−MS (positive): calcd for $C_{48}H_{24}N_8S_3Fe_2^+$ [M$^+$], 919.9985; found: 919.9994. Anal. Calcd for $C_{48}H_{24}N_8S_3Fe_2$: C, 62.62; H, 2.63; N, 12.17. Found: C, 62.50; H, 2.72; N, 12.11.

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[20] The spectroelectrogram measurements were carried out by using a two-electrode configuration with a Pt mesh and a wire as the working and counter electrodes, respectively, which were separated by a glass filter. A constant-current reduction and oxidation were applied to the sample solution. The electrical current was monitored by a microampere meter. The potential values are automatically increased by the resistance of the sample solution from 0 up to ±12 V, but the potential values could not be monitored by our constant current apparatus.

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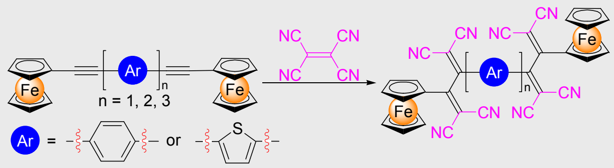

Aryl-substituted 1,1,4,4-tetracyano-1,3-butadienes and bis(1,1,4,4-tetracyanobutadiene)s, possessing a ferrocenyl group on each terminal, were prepared by the reaction of corresponding alkynes with tetracyanoethylene in a [2 + 2] cycloaddition– retroelectrocyclization reaction. The redox behavior of novel FcTCBDs was examined by cyclic voltammetry and differential pulse voltammetry, which revealed their properties of multi-electron transfer depending on the number of ferrocene and TCBD moieties. Moreover, significant color changes were observed by visible spectroscopy under the electrochemical reduction conditions.

Donor-acceptor chromophores

Taku Shoji, Akifumi Maruyama, Chisa Yaku, Natsumi Kamata, Shunji Ito, Tetsuo Okujima and Kozo Toyota*

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Synthesis, Properties and Redox Behavior of 1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadienes Connected by Aryl, Biaryl and Teraryl Spacers