Donor–Acceptor Systems

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 (FcTCBDs) and bis(1,1,4,4-tetracyanobutadiene)s (bis-FcTCBDs), possessing a ferrocenyl group on each terminal, were prepared by the reaction of a variety of alkynes with tetracyanoethylene (TCNE) in a [2+2] cycloaddition reaction, followed by retro-electrocyclization 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 inves-

tigated by using UV/Vis spectroscopy. The redox behaviors of FcTCBDs and bis-FcTCBDs were 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.

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-retro-

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electrocyclization (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 ferrocenecontaining 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 multistep 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 be strongly 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

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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 new 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. ¹H NMR chemical shifts and the melting point of the products confirmed the formation of the ethynylferrocene derivatives 2-10 shown in the literatures. Moreover, El mass spectra of the products showed the correct molecular ion peaks as $[M]^+$ ions (see the Supporting Information). Thus, these alkyne derivatives were utilized in further transformations for the synthesis of the new FcTCBD and bis-FcTCBD derivatives.

For the synthesis of the new 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 CH₂Cl₂ at room temperature yielded **11** in



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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.



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

97% yield as a sole product. The reaction of 3,^[8] which has an electron-donating *N*,*N'*-dimethylamino group at the *para* position on the benzene ring, with TCNE in CH₂Cl₂ gave 12 in 91% yield. Alkyne derivative 4,^[9] which possesses a nitro group at the *para* 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 a highly electron-donating group in the alkyne terminal is required for the [2+2] CA–RE

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reaction with TCNE to succeed. Similar to the results on the aryl derivatives, the [2+2] CA-RE reaction of the thiophene derivative 5^[9] with TCNE in CH₂Cl₂ 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 CH₂Cl₂ at the reflux temperature (Scheme 1). Bis-FcTCBD chromophores 17 and 18, each bearing a biarylene spacer, were obtained in 99 and 99% yields, respectively, by the [2+2] CA-RE reaction of bis(ethynylferrocene) precursors ${\bm 8}^{[12]}$ and ${\bm 9}^{[12]}$ with TCNE (Scheme 2). Bis-FcTCBD 19, connected with a 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

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The new FcTCBDs and bis-FcTCBDs 11-19 were fully characterized based on their spectral data, as summarized in the Experimental Section. The NMR spectroscopic 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 $\tilde{\nu}_{max}$ = 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 $\lambda_{max}\!=\!621$ and 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 $\lambda_{max} = 632 \text{ nm}$ in CH₂Cl₂ (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, the UV/Vis spectrum of the FcTCBD 12 with N,N'-dimethylanilino substituent exhibited a strong absorption band at $\lambda_{max} = 469$ 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 $(\lambda_{max} = 481 \text{ nm})^{[14]}$ with *N*,*N*'-dimethylanilino substituent. 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 $\lambda_{max} = 627$ nm, which should correspond to that of FcTCBDs 11-13, arising from the ICT from ferrocene to the TCBD unit.

UV/Vis spectra of bis-FcTCBDs 15 and 17 connected by 1,4phenylene and 4,4'-biphenylene spacers revealed a broad absorption band at $\lambda_{max} = 616$ nm in DMSO^[15] and $\lambda_{max} = 626$ nm



Figure 1. UV/Vis spectra of 11 (-—), 12 (——), and 13 (----) in CH₂Cl₂.



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

in CH2Cl2, respectively, which reached to the 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. The 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.

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 new 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/AgNO3 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

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Figure 3. UV/Vis spectra of 14 (____), 16 (____), 18 (-----), and 19 (-----) in $CH_2Cl_2.$

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/AgNO₃) of **11–19** measured under a scan rate of 100 mV s⁻¹ are summarized in Table 2.

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

Table 2. R the bis-FcT	edox potentia CBD derivativ	Is ^[a,b] of the F res 15–19 .	cTCBD deriva	tives 11–14 a	nd 20 and
Sample	Method	E_1^{ox}	$E_1^{\rm red}$	$E_2^{\rm red}$	$E_3^{\rm red}$
		[V]	[V]	[V]	[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 ^[5b]	CV	+0.58	-0.60		
	(DPV)	(+0.56)	(-0.58)	(-0.98)	_

[a] V versus Ag/AgNO₃, 1 mm in benzonitrile containing Et₄NClO₄ (0.1 m), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mV s⁻¹ and internal reference (Fc/Fc⁺ = +0.15 V). [b] Half-wave potentials E^{ox} and $F^{\text{red}} = (E_{\text{pc}} + E_{\text{pa}})/2$ on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.



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

first oxidation potential of FcTCBDs **11–14** and bis-FcTCBDs **15–19** was observed at a similar potential region (+0.55 to + 0.61 V) on CV under the electrochemical oxidation, which resembles that of much simpler FcTCBD **20** (+0.58 V).^[5b] 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 para 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 and -1.05 V on CV, which should also be attributed to the stepwise formation of a radical anionic and a dianionic species, respectively.

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 species up to the tetraanions. Bis-FcTCBDs 15 (-0.60, -0.75, and -1.18 V) and 16 (-0.39, -0.66, and -1.27 V; Figure 4) 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

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Figure 4. Cyclic voltammogram of the reduction of **16** (1 mm) in benzonitrile containing Et_4NCIO_4 (0.1 m) as a supporting electrolyte; scan rate = 100 mV s⁻¹.

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.

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 new hybrid structures of violenes and cyanines during the study on the synthesis and redox behavior of TCBDs and DCNQs substituted by ferrocene,^[5] azulene,^[18] and 2H-cyclohepta[b]furan-2-one^[6,19] moieties, in addition to the Hünig's violene-cyanine hybrid structure. Similar to the TCBDs and DCNQs derivatives reported by us previously, new 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_4NCIO_4 (0.1 M) as a 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, a 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 yellowcolored 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 and 725 nm, which spread into the near-infrared region, gradually developed (Figure 5). The reverse oxidation decreased the new absorption bands, and regenerated the original absorption bands of **16**.

Visible spectra of bis-FcTCBD 17 with a 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 a bithiophenediyl spacer (Figure 6). 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 connect-



Figure 5. Continuous change in the UV/Vis spectrum of **16** under constantcurrent electrochemical reduction (100 μ A) in benzonitrile containing Et₄NClO₄ (0.1 μ) at 20 s intervals.

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Figure 6. Continuous change in the UV/Vis spectrum of 18 under constantcurrent electrochemical reduction (100 μ A) in benzonitrile containing Et₄NClO₄ (0.1 m) at 20 s intervals.

ed 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 retro-electrocyclization 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 new 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 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.

Syntheses

1,1,4,4-Tetracyano-2-ferrocenyl-3-phenyl-1,3-butadiene (11): TCNE (64 mg, 0.50 mmol) was added to a solution of 2 (100 mg, 0.35 mmol) in CH₂Cl₂ (10 mL). 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 CH₂Cl₂/EtOAc (20:1) to give 11 (140 mg, 97%) as blue crystals. M.p. > 300 °C (CH₂Cl₂/ hexane); ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H} = 7.63 - 7.60$ (m, 3 H, *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, 1 H, J=1.5, 1.5 Hz, Fc), 4.38 ppm (s, 5 H, Cp); ¹³C NMR (125 MHz, CDCl₃): $\delta_{C} = 172.3$ (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 ppm (Fc); IR (KBr disk): $\tilde{\nu}_{\rm max}\!=\!2957$ (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 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (log ϵ) = 284 (sh) (4.13), 327 (4.23), 472 (sh) (2.94), 621 nm $(3.40 \text{ dm}^3 \text{ m}^{-1} \text{ cm}^{-1})$; HR-FABMS (positive): m/z calcd for C₂₄H₁₄N₄Fe: 414.0568 [M⁺]; found: 414.0588; elemental analysis 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): TCNE (58 mg, 0.45 mmol) was added to a solution of 3 (100 mg, 0.30 mmol) in CH₂Cl₂ (10 mL). 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 CH₂Cl₂/ EtOAc (20:1) to give 12 (125 mg, 91%) as reddish-brown crystals. M.p. 204–205 °C (CH₂Cl₂/hexane); ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H} =$ 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, 1 H, J=1.5, 1.5, 1.5 Hz, Fc), 4.67 (dd, 1 H, J=1.5, 1.5 Hz, Fc), 4.44 (s, 5 H, Cp), 3.12 ppm (s, 6 H, NMe₂); ¹³C NMR (125 MHz, CDCl₃): $\delta_{c} = 174.6$ (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 ppm (NMe₂); IR (KBr disk): $\tilde{\nu}_{\rm max}\!=\!2925$ (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 cm $^{-1}$ (m); UV/Vis (CH $_2 Cl_2$): λ_{max} (log ε) = 247 (4.26), 284 (4.11), 324 (sh) (4.08), 349 (4.20), 411 (4.21), 469 (4.45), 626 nm (sh) (3.45 dm³ M^{-1} cm⁻¹); HR-FABMS (positive): m/z calcd for C₂₆H₁₉FeN₅⁺: 457.0990 [*M*⁺]; found: 457.0972; elemental analysis calcd (%) for C₂₆H₁₉FeN₅: C 68.29; H 4.19; N 15.31; found: C 68.20; H 4.25; N 15.26.

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p-(1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadien-3-yl)nitroben-

zene (13): TCNE (62 mg, 0.48 mmol) was added to a solution of 4 (104 mg, 0.31 mmol) in CH₂Cl₂ (5 mL). 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 CH₂Cl₂/EtOAc (20:1) to give **13** (135 mg, 95%) as a blue oil. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H} = 8.34$ (d, 2 H, J = 9.0 Hz, *m*-Ph), 7.72 (d, 2 H, 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, 1 H, J=1.5, 1.5, 1.5 Hz, Fc), 4.47 (s, 5 H, Cp), 4.42 ppm (brs, 1 H, Fc); ¹³C NMR (125 MHz, CDCl₃): $\delta_c = 171.1$ (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 ppm (Fc); one signal of Fc is overlapped with the other signal. IR (KBr disk): $\tilde{\nu}_{max}$ = 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 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 272 sh (4.31), 308 (4.40), 360 sh (4.11), 525 sh (3.16), 627 nm $(3.40 \text{ dm}^3 \text{ m}^{-1} \text{ cm}^{-1})$; HR-FABMS (positive): m/z calcd for C₂₄H₁₃N₅O₂Fe⁺: 459.0419 [*M*⁺]; found: 459.0401; elemental analysis calcd (%) for $C_{24}H_{13}N_5O_2Fe\colon$ 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): TCNE (65 mg, 0.51 mmol) was added to a solution of 5 (100 mg, 0.34 mmol) in CH₂Cl₂ (10 mL). 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 CH₂Cl₂/EtOAc (20:1) to give **14** (130 mg, 91%) as a blue oil. ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ =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, 1 H, 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 ppm (s, 5 H, Cp); ^{13}C NMR (125 MHz, CDCl_3): $\delta_{\text{C}}{=}$ 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 ppm (Fc); IR (KBr disk): $\tilde{\nu}_{max} = 3106$ (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 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (log ε)=309 (sh) (4.14), 358 (4.37), 498 (sh) (3.12), 627 nm (3.43 dm³ μ⁻¹ cm⁻¹); HR-FABMS (positive): m/z calcd for $C_{22}H_{12}FeN_4S^+$: 420.0132 [M^+]; found: 420.0133; elemental analysis calcd (%) for C₂₂H₁₂FeN₄S: 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): TCNE (103 mg, 0.80 mmol) was added to a solution of 6 (134 mg, 0.27 mmol) in CH₂Cl₂ (8 mL). The resulting mixture was heated at reflux 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 $CH_2CI_2/EtOAc$ (20:1) to give 15 (144 mg, 71%) as green crystals. M.p. 250°C decomp. (MeCN); ¹H NMR (500 MHz, [D₆]acetone): $\delta_{\rm H} = 8.23$ (s, 2 H, 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 ppm (s, 5H, Cp). Low solubility hampered the measurement of the ¹³C NMR spectrum; IR (KBr disk): $\tilde{\nu}_{max}$ = 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 cm $^{-1}$ (m); UV/Vis (DMSO): $\lambda_{\rm max}$ (log $\varepsilon)\!=\!255$ (4.59), 353 (4.47), 474 (4.60), 616 nm (3.65 dm³ M⁻¹ cm⁻¹); HR-ESIMS (positive): m/z calcd for $C_{42}H_{22}Fe_2N_8 + Na^+$: 773.0558 [M+Na⁺]; found: 773.0558; elemental analysis calcd (%) for $C_{42}H_{22}Fe_2N_8$ ·H₂O: 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)thio-

phene (16): TCNE (79 mg, 0.62 mmol) was added to a solution of 7 (100 mg, 0.20 mmol) in CH₂Cl₂ (8 mL). The resulting mixture was heated at reflux 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 $^\circ\text{C}$ decomp. (CH₂Cl₂/hexane); ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 7.71 (s, 1 H, 3,4-H of Th), 7.55 (s, 1H, 3,4-H of Th), 5.59 (brs, 2H, Fc), 5.13 (brs, 2H, Fc), 4.94 (brs, 2H, Fc), 4.50 (s, 5H, Cp), 4.49 (s, 5H, Cp), 4.36 ppm (br s, 2 H, Fc); 13 C NMR (125 MHz, CDCl₃): $\delta_{C} = 170.6$ (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 ppm (Fc); IR (KBr disk): $\tilde{\nu}_{\rm max}\!=\!3110$ (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 cm $^{-1}$ (w); UV/Vis (CH $_2 \text{Cl}_2$): λ_{max} (log $\varepsilon)\!=\!262$ (4.41), 350 (4.56), 410 (4.51), 437 (4.38), 611 nm (3.78 dm³ μ⁻¹ cm⁻¹); HR-FABMS (positive): m/z calcd for $C_{40}H_{20}N_8SFe_2^+$: 756.0230 [M^+]; found: 756.0215; elemental analysis 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): TCNE (77 mg, 0.60 mmol) was added to a solution of **8** (136 mg, 0.23 mmol) in CH_2CI_2 (6 mL). The resulting mixture was heated at reflux 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 CH₂Cl₂/EtOAc (20:1) to give 17 (188 mg, 99%) as dark-green crystals. $M.p. > 300 \degree C$ (CH₂Cl₂/hexane); ¹H NMR (500 MHz, [D₆]acetone): $\delta_{\rm H}$ = 8.10 (d, 4 H, 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 (brs, 2H, Fc), 4.96 (m, 2H, Fc), 4.36 ppm (s, 10 H, Cp); ¹³C NMR (125 MHz, [D₆]acetone): $\delta_{C} = 171.7$ (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 ppm (Fc); IR (KBr disk): $\tilde{\nu}_{max}$ = 3096 (w), 2222 (m, C=N), 1518 (s), 1423 (s), 1382 (w), 1338 (w), 1314 (m), 1291 (m), 1272 (w), 1178 (w), 1106 (w), 1073 (w), 1001 (w), 936 (w), 835 (m), 803 (m), 751 (w), 735 (w), 665 cm $^{-1}$ (w); UV/Vis (CH $_2 Cl_2$): λ_{max} (log $\varepsilon)\!=\!315$ (sh) (4.51), 360 (4.70), 500 (sh) (3.36), 626 nm (3.65 dm³ μ⁻¹ cm⁻¹); HR-FABMS (positive): m/z calcd for $C_{48}H_{26}N_8Fe_2^+$ [M^+], 826.0979; found: 826.0981; elemental analysis calcd (%) for C48H26N8Fe2: 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)**: TCNE (65 mg, 0.51 mmol) was added to a solution of **9** (100 mg, 0.17 mmol) in CH₂Cl₂ (6 mL). The resulting mixture was heated at reflux 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 CH₂Cl₂/EtOAc (20:1) to give **18** (141 mg, 99%) as purple crystals. M.p. > 300°C (CH₂Cl₂/ hexane); ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ =7.67 (dd, 2H, *J*=4.0, 4.0 Hz, 3-H of Th), 7.35 (brs, 2H, 4-H of Th), 5.54 (brs, 2H, Fc), 5.06 (brs, 2H, Fc), 4.87 (brs, 2H, Fc), 4.50 (s, 10H, Cp), 4.48 ppm (brs, 2H, Fc); ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ =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 (CN), 112.5

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(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 ppm (Fc); IR (KBr disk): $\tilde{\nu}_{\rm max}\!=\!3094$ (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 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 251 (4.41), 337 (4.48), 476 (4.72), 496 (sh) (4.69), 620 nm (sh) (3.78 dm³ m⁻¹ cm⁻¹); HR-FABMS (positive): m/z calcd for C₄₄H₂₂Fe₂N₈S₂⁺: 838.0108 [M^+]; found: 838.0082; elemental analysis calcd (%) for $C_{44}H_{22}Fe_2N_8S_2H_2O$: 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): TCNE (192 mg, 1.50 mmol) was added to a solution of 10 (332 mg, 0.50 mmol) in CH₂Cl₂ (5 mL). The resulting mixture was heated at reflux 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 CH₂Cl₂/EtOAc (20:1) to give 19 (437 mg, 95%) as purple crystals. M.p. 172–175 °C (CH₂Cl₂/hexane); ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H} =$ 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 ppm (s, 10H, Cp); ¹³C NMR (125 MHz, CDCl₃): $\delta_{c} = 171.9$ (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 ppm (Fc);IR (KBr disk): $\tilde{\nu}_{max}$ = 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 cm $^{-1}$ (w); UV/Vis (CH_2Cl_2): $\lambda_{\rm max}$ (log ε) = 256 (sh) (4.49), 285 (sh) (4.43), 332 (4.52), 532 nm (4.83 dm³ μ^{-1} cm⁻¹); HR-FABMS (positive): m/z calcd for C₄₈H₂₄N₈S₃Fe₂⁺: 919.9985 [*M*⁺]; found: 919.9994; elemental analysis calcd (%) for C48H24N8S3Fe2: C 62.62; H 2.63; N 12.17; found: C 62.50; H 2.72; N 12.11.

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FULL PAPER



Donor–acceptor chromophores: Arylsubstituted 1,1,4,4-tetracyano-1,3-butadienes (FcTCBDs) and bis(1,1,4,4-tetracyanobutadiene)s (bis-FcTCBDs), possessing a ferrocenyl group on each terminal, were prepared by a [2+2] cycloaddition-retro-electrocyclization reaction (see scheme).

Donor–Acceptor Systems

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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