

Synthesis, Properties, and Redox Behavior of Ferrocenyl-1,1,4,4-tetracyano-1,3-butadienes Connected by Arylamine and Azobenzene Spacers

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Ferrocene-substituted 1,1,4,4-tetracyano-1,3-butadienes (FcTCBDs) connected by arylamine and azobenzene spacers were prepared by the reaction of a variety of alkynes with tetracyanoethylene (TCNE) in a [2 + 2] cycloaddition, followed by retroelectrocyclization of the initially formed [2 + 2] cycloadducts (i.e., cyclobutene derivatives). The characteristic intramolecular charge transfer (ICT) from the donors (ferrocene and arylamine) to the acceptor (TCBD) moieties was investigated by using UV–vis spectroscopy. The redox behaviors of the FcTCBDs were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which revealed their promising redox properties with multi-electron transfer depending on the number of FcTCBD moieties in the molecules. Moreover, significant color changes were observed by visible spectroscopy under the electrochemical reduction conditions.

Introduction

Ferrocene has attracted interest due to its facile redox properties, with a rather low oxidation potential that allows it to form a stabilized positively charged 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 amphoteric redox properties have been extensively studied.¹

In 2002, Mochida and Yamazaki reported that the reaction of ethynylferrocene derivatives with tetracyanoethylene (TCNE) afforded formal [2 + 2] cycloaddition products, namely, cyclobutene derivatives, which exhibited a ring-opening reaction to give the corresponding ferrocenyl-1,1,4,4-tetracyano-1,3butadienes (FcTCBDs).² In recent years, several groups have reported the synthesis and properties of FcTCBD derivatives connected with various π -electron systems.³ Especially, Diederich et al. have extensively studied these types of molecules as a new class of ICT chromophores.⁴ A variety of FcTCBD derivatives, which exhibit promising nonlinear optical properties, have been prepared by the reaction of alkynes and butadiynes substituted by the ferrocenyl group with TCNE.

We have also reported the synthesis and electrochemical properties of TCBD derivatives with various aromatic substituents (e.g., azulenyl,⁵ arylamino,⁶ 2-oxo-2*H*-cyclohepta[*b*]-3-furyl,⁷ and ferrocenyl⁸ groups) by the [2 + 2] cycloaddition–

retroelectrocyclization (CA-RE) of the corresponding alkynes with TCNE. Especially, TCBD derivatives substituted by arylamino⁶ and ferrocenyl⁸ groups showed electrochromic properties with rather high reversibility in the redox cycles. For this reason, the TCBD derivatives with both ferrocenyl and arylamino groups should exhibit highly stabilized redox cycles and improve their electrochromic properties, rather than TCBD derivatives substituted by either ferrocenyl or arylamino group. Moreover, systematic investigation of the effect of the arylamine cores toward the FcTCBD derivatives has not yet been explored, although the optical and electrochemical properties of the TCBD derivatives could be strongly affected by the substituted π -electron systems. An intensive investigation of the effect of arylamine cores connected to the FcTCBD units should provide useful information for the creation of electronic devices utilizing their amphoteric redox properties.

Herein, we describe the palladium-catalyzed synthesis of ferrocene-substituted alkyne derivatives connected by several arylamine cores and the transformation to that with an azobenzene core, as well as the application of the alkyne derivatives to the [2 + 2] CA–RE reaction with TCNE to afford novel FcTCBD derivatives. The electronic properties of the novel FcTCBD derivatives connected by the arylamine cores in addition to that with an azobenzene core were examined by absorption spectroscopy, electrochemical analysis, and spectroelectrochemical measurements.

Results and Discussion

Synthesis. Preparation of ethynylferrocene derivatives with arylamine core 2-5 was accomplished by palladium-catalyzed alkynylation of iodoarylamines with ethynylferrocene (1) under Sonogashira–Hagihara conditions.⁹ Synthesis of azobenzene derivative 6 was also established by Cu-catalyzed homocoupling of 2 under the conditions reported by Zhang and Jiao.¹⁰

Cross-coupling of **1** with 4-iodoaniline in the presence of $[Pd(PPh_3)_4]$ catalyst in Et₃N/THF at 50 °C afforded 4-(ferrocenylethynyl)aniline (**2**) in 58% yield (Scheme 1).¹¹ Crosscoupling of **1** with 4,4'-diiododiphenylamine using $[Pd(PPh_3)_4]$ as a catalyst and subsequent chromatographic purification on silica gel afforded the desired 4,4'-bis(ferrocenylethynyl)diphenylamine (**3**) in 65% yield (Scheme 2). Sonogashira– Hagihara reaction of **1** with 3,6-diiodocarbazole afforded **4** in 96% yield (Scheme 3). Tris-adduct **5** was also prepared by the reaction of **1** with 4,4',4''-triiodotriphenylamine in 95% yield (Scheme 4).¹² Azobenzene derivative **6** was obtained by oxidative coupling of compound **2** in the presence of CuBr/pyridine catalyst in almost quantitative yield (99%, Scheme 5).

For the synthesis of the FcTCBD derivatives connected by arylamine core, the [2 + 2] CA–RE reaction of **2–6** with TCNE was conducted according to the previously described procedure.^{2–8} The reaction of **2** with TCNE in CH₂Cl₂ at room temperature yielded **7** in 64% yield (Scheme 1). Bis-FcTCBD chromophores **8** and **9**, which bear diphenylamine and carbazole spacer, were obtained in 87% and 93% yields, respectively, by the [2 + 2] CA–RE of bis(ethynylferrocene) pre-

cursors 3 and 4 with TCNE (Schemes 2 and 3). Tris-FcTCBD 10 with a triphenylamine core was also obtained in 81% yield by the [2 + 2] CA–RE reaction of the corresponding tri-alkyne 5 with TCNE (Scheme 4). The reaction of 6 with TCNE in CH₂Cl₂ gave 11 in 59% yield in spite of the existence of an electron-withdrawing azo group between the para positions on the two benzene rings (Scheme 5).

Spectroscopic Properties. These new FcTCBDs 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 7–11 ionized by FAB showed the correct molecular ion peaks. The characteristic stretching vibration band of the C \equiv N moiety of the FcTCBDs 7–11 was observed at $v_{max} = 2222-2226 \text{ cm}^{-1}$ in their IR spectra. These results are consistent with the structures of the products. UV–vis spectra of FcTCBDs 7–11 are shown in Figure 1. The absorption maxima and coefficients (log ε) of the FcTCBDs 7–11 in CH₂Cl₂ and in the mixed hexane solvent with certain amounts of CH₂Cl₂ to maintain their solubility are summarized in Table 1.

UV–vis spectra of FcTCBDs 7–11 showed characteristic weak absorption bands arising from the presumed ICT absorption between ferrocene and TCBD units in the visible region. Absorption bands in the visible region of these compounds displayed slight bathochromic shifts, along with the increment of extinction coefficients with the number of substituted FcTCBD unit. These results suggest that multiple FcTCBD moieties with arylamine cores expand the π -conjugation through the nitrogen atom of central arylamine cores. When the solvent was changed from CH₂Cl₂ to the mixed CH₂Cl₂/



Scheme 1. Synthesis and [2 + 2] CA–RE reaction of compound 2.



Scheme 2. Synthesis and [2 + 2] CA–RE reaction of compound 3.



Scheme 3. Synthesis and [2 + 2] CA–RE reaction of compound 4.



Scheme 4. Synthesis and [2 + 2] CA–RE reaction of compound 5.



Scheme 5. Synthesis and [2 + 2] CA–RE reaction of compound 6.



Figure 1. UV-vis spectra of 7 (blue line), 8 (red line),9 (green line), 10 (purple broken line), and 11 (light-blue broken line) in CH₂Cl₂.

hexane solvent, the FcTCBD derivatives 7–11 showed hypsochromical solvatochromism.

A noticeable spectral feature of 7 is the presence of a distinct absorption band at 617 nm in CH₂Cl₂, in which compound 7 exhibits hypsochromic shift by 20 nm ($\lambda_{max} = 597$ nm) in the less polar 10% CH₂Cl₂/hexane, suggesting the ICT nature of this band.¹³ Bis-FcTCBD 9, with a carbazole core, exhibits a broad absorption band at $\lambda_{max} = 631$ nm. Whereas, bis-FcTCBD 8 and tris-FcTCBD 10 shows a strong absorption band (8: $\lambda_{max} = 475$ nm; 10: $\lambda_{max} = 480$ nm) along with a broad absorption similar with that of FcTCBDs 7 and 9.

Previously, Mochida et al. reported that simpler FcTCBD derivative **12** exhibits a broad absorption centered at $\lambda_{max} = 632 \text{ nm}$ in CH₂Cl₂ (Figure 2).² More recently, we have also

Table 1. Absorption maxima [nm] and their coefficients $(\log \varepsilon)$ in visible region of the FcTCBDs 7–11 in CH₂Cl₂ and in hexane^{a)}, along with those of FcTCBDs 12–14 as references

Sample	λ_{\max} (log ε) in CH ₂ Cl ₂	λ_{\max} (log ε) in hexane
7	421 (4.29), 617 (3.41)	403 (4.28), 597 (3.35) ^{b)}
8	475 (4.71), 620 (3.76)	461 (4.71), 610 (3.76) ^{c)}
9	423 (4.32), 631 (3.62)	414 (4.32), 621 (3.55) ^{c)}
10	480 (4.64), 624 (3.82)	469 (4.64), 610 (3.81) ^{c)}
11	615 (3.65)	600 (3.62) ^{b)}
12 ²	632 (3.32)	
13 ¹⁴	481 (3.85)	
14 ^{8c}	469 (4.45), 626 (3.45)	

a) CH_2Cl_2 was added to hexane to maintain solubility of the compounds. b) Measured in 10% CH_2Cl_2 /hexane. c) Measured in 30% CH_2Cl_2 /hexane.

reported that the FcTCBD **14** with *N*,*N'*-dimethylanilino substituent showed a broad absorption band at $\lambda_{max} = 626$ nm in CH₂Cl₂.^{8c} Thus, the longest wavelength absorption band of the FcTCBDs **7–10** could be ascribed to the ICT absorption from ferrocene to the TCBD units.

On the other hand, the longest wavelength absorption of **8** and **10** resembles with that of TCBD **13** $(\lambda_{max} = 481 \text{ nm})^{14}$ and FcTCBD **14** $(\lambda_{max} = 469 \text{ nm})^{8c}$ with *N*,*N'*-dimethylanilino substituent in the λ_{max} value. Therefore, the strong absorption band at around 480 nm of the FcTCBDs **8** and **10** should be ascribed to the ICT from arylamine moiety to the TCBD units as shown in Scheme 6. In contrast compound **9** did not show such a strong absorption band in the region probably due to the less effective conjugation between the TCBD moieties and the lone pair electrons of the nitrogen atom on the carbazole. Bis-FcTCBD **11** showed a broad absorption band centered at



Figure 2. TCBD derivatives with ferrocene and N,N-dimethylaniline substituent.



Scheme 6. Plausible redox behavior of compound 8.

 $\lambda_{\text{max}} = 615 \text{ nm}$ and also strong absorption band at $\lambda_{\text{max}} = 364$ nm that should correspond to the absorption of azobenzene moiety.

Electrochemistry. To clarify the effect on the electrochemical properties of aromatic substituents on the FcTCBD derivatives 7–11, the redox behavior of the FcTCBD chromophores 7–11 was examined by CV and DPV. Cyclic voltammograms of FcTCBDs 7 and 10 are shown in Figures 3 and 4, respectively. Plausible redox behavior of FcTCBD 8 under the electrochemical reduction conditions is illustrated in Scheme 6. The redox potentials (in volts vs. Ag/AgNO₃) of 7–11 measured under a scan rate of 100 mV s⁻¹ are summarized in Table 2.

All of the FcTCBD chromophores 7–11 displayed 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. The first oxidation wave of the FcTCBDs 7–11 was observed at a similar potential region (+0.54 to +0.58 V) on CV under the electrochemical oxidation, which resembles that of simpler FcTCBD 12 (+0.58 V).² Thus, it should be concluded that there is a less effective interaction between the ferrocene and arylamine units separated by the TCBD unit, from the view point of their oxidation potentials. In contrast to the oxidation, the reduction of 7–11 was significantly affected by the nature of core units, e.g., arylamine and azobenzene cores, connected to the FcTCBD unit. FcTCBD chromophore 7 displayed a





reversible two-stage reduction waves at -0.91 and -1.16 V (Figure 3).

A reversible three-stage wave was observed by CV in bis-FcTCBD 8 (-0.78, -0.86, and -1.12 V), in which the third reduction wave was a two-electron transfer in one step to form a tetraanionic species. Electrochemical reduction of 9 showed a reversible two-step reduction wave with half-wave potentials of -0.81 and -1.12 V, which could be attributed to the formation of a radical dianionic and a tetraanionic species. Although the bis-FcTCBD **8** has a symmetrical structure, two TCBD units showed a stepwise reduction by CV, which should be attributed to the stepwise reduction to a tetraanionic species as shown in Scheme 6.^{2,8c} This means the existence of redox interaction between the intramolecular two FcTCBD moieties through the diphenylamine spacer. On the other hand, bis-FcTCBD **9** displayed a two-step reduction wave, with respect to its symmetrical structure. This result might be implied to the less effective conjugation between the two FcTCBD units through the carbazole spacer.

The electrochemical reduction of tris-FcTCBD **10** also exhibited a reversible three-step reduction wave, whose potentials were identified as -0.73, -0.83, and -1.10 V by CV as half-wave potentials (Figure 4). Recently, we reported the first reduction potential of FcTCBDs **14–16** was dependent on the nature of the para substituent on the aromatic ring.^{8c} In this



Figure 4. Cyclic voltammogram of the reduction of 10 (1.0 mM) in benzonitrile containing Et₄NClO₄ (0.10 M) as a supporting electrolyte; scan rate: 100 mV s⁻¹.

case, since the first reduction potential of the FcTCBDs 7–11 decreased according to the number of TCBD units in the molecules, the connected TCBD units behaved as electron-withdrawing group and increased the electron accepting property by effective conjugation through the central arylamine cores. Bis-FcTCBD 11 with an azobenezene core exhibited less negative first reduction potential on CV (-0.67 V), compared with those of bis-FcTCBDs 7–10. Moreover, first reduction potential of bis-FcTCBD 11 is comparable to that of FcTCBD 16 (-0.64 V) with an electron-withdrawing *p*-nitro substituent. These results should be ascribed to the electron-withdrawing nature of the azobenzene core.

Electrochromism is observed in reversible redox systems that exhibit significant color changes in different oxidation states. Stabilization of the redox cycle is very important in the construction of electrochromic materials because the molecules that are utilized for this application require high redox stabilities.¹⁵

We have reported the synthesis of various redox-active TCBD chromophores with the aim of creating stabilized electrochromic materials.¹⁶ In these studies, we found the FcTCBD units connected with the π -electron systems exhibited electrochromism with rather high reversibility in which the strong absorption bands spread into visible and/or nearinfrared regions under the electrochemical reduction conditions.⁸ Similar to the FcTCBD derivatives reported by us previously, these FcTCBDs 7-11 should become another example of the redox systems as the extension of the hybrid structures of violenes and cvanines with multi-electron transfer proposed by Hünig et al.¹⁷ Thus, the visible spectra of 7–11 were monitored to clarify the color changes during the electrochemical reactions. Constant-voltage oxidation and reduction was applied to the solutions of 7-11 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 a supporting

Sample	Method	E_1^{ox}/V	E_2^{ox}/V	$E_1^{\rm red}/{\rm V}$	$E_2^{\rm red}/{\rm V}$	$E_3^{\rm red}/{\rm V}$
7	CV	+0.54	_	-0.91 (1e ⁻)	-1.16 (1e ⁻)	
	(DPV)	(+0.52)	(+1.08)	(-0.89)	(-1.14)	
8	CV	+0.57		$-0.78 (1e^{-})$	$-0.86 (1e^{-})$	-1.12 (2e ⁻)
	(DPV)	(+0.55)	(+1.21)	(-0.76)	(-0.84)	(-1.10)
9	CV	+0.57		$-0.81 (2e^{-})$	-1.12 (2e ⁻)	
	(DPV)	(+0.55)	(+1.24)	(-0.79)	(-1.10)	
10	CV	+0.57		-0.73 (2e ⁻)	$-0.83 (1e^{-})$	$-1.10 (3e^{-})$
	(DPV)	(+0.55)	(+1.26)	(-0.71)	(-0.81)	(-1.08)
11	CV	+0.58		-0.67 (2e ⁻)	-1.08 (2e ⁻)	
	(DPV)	(+0.56)		(-0.65)	(-1.06)	(-1.73)
14 ^{8c}	CV	+0.55		-0.95	-1.20	
	(DPV)	(+0.53)		(-0.93)	(-1.18)	
15 ^{8c}	CV	+0.59		-0.78	-1.10	
	(DPV)	(+0.57)		(-0.76)	(-1.08)	
16 ^{8c}	CV	+0.61		-0.64	-0.97	
	(DPV)	(+0.59)		(-0.62)	(-0.95)	

Table 2. Redox potentials^{a),b)} of the FcTCBD derivatives 7-11

a) V versus Ag/AgNO₃, 1.0 mM in benzonitrile containing Et₄NClO₄ (0.10 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 $E_{\text{red}} = (E_{\text{pc}} + E_{\text{pa}})/2$ on CV, E_{pc} , and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.



Figure 5. Continuous change in the visible spectrum of **8** under constant voltage electrochemical reduction (-1.00 V, top) and further electrochemical reduction (-1.50 V, bottom) in benzonitrile containing Et₄NClO₄ (0.10 M) at 20 s intervals.

electrolyte at room temperature under the electrochemical reaction conditions.

The absorption band of 7 in the visible region gradually increased and the color of the solution changed from green to yellow during the electrochemical reduction at -1.08 and -1.40 V (Figures S-15, top). Reversible oxidation of the yellow solution regenerated the original color and spectrum of the compound along with the isosbestic point at 495 nm (Figure S-15, bottom). Similarly, the green color of the solution of bis-FcTCBD 8 changed to pale-blue during the electrochemical reduction at -1.00 V, and further reduction at -1.50 V of the pale-blue solution turned to deep-blue together with the development of absorption at around 750 nm (Figure 5). Reversible oxidation of the deep-blue solution exhibited further development of the new absorption band at around 750 nm, instead of the regeneration of the original spectrum of the compound. When the UV-vis spectrum of bis-FcTCBD 9 was measured under the electrochemical reduction conditions (-1.00 V), a new absorption band in the visible region at around 630 nm gradually developed. Following the spectral change, further two-stage color changes were observed in the visible spectra of 9 by the electrochemical reduction at

-1.50 V. At the beginning in the two-stage color changes, new absorptions in the visible region at 630 nm gradually developed in a different way by the reduction at -1.00 V, and the new absorption band was gradually decreased by further reduction at the same voltage (Figures S-19, top). Although good reversibility was observed by CV, reverse oxidation of the reduced solution did not regenerate the spectrum of 9 (Figures S-19, bottom). The poor reversibility for the electrochromisms of 8 and 9 might be attributable to the decomposition of the anionic species produced by the electrochemical reduction, instead of regeneration of the parents 8 and 9. When the visible spectra of tris-FcTCBD 10 were monitored under the electrochemical reduction conditions at -1.00 and -1.50 V, the absorption band in the visible region that spread into the near-infrared region gradually developed along with a color change from brown to pale yellow (Figures S-21, top). Reverse oxidation of the reduced species regenerated the original color of 10 (Figure S-21, bottom). Reversible color change from red to blue was observed in bis-FcTCBD 11 with an azobenzene spacer. The absorption band in the visible region of 11 gradually increased with the development of new absorption bands in the near-infrared region along during the electrochemical reduction at -1.00 and -1.50 V. Reverse oxidation of the reduced species decreased the new absorption bands, along with recovery of the original spectrum of 11.

Conclusion

A series of ethynylferrocene derivatives 2-5 with an arylamine core were prepared by palladium-catalyzed Sonogashira-Hagihara reaction. The derivative with azobenzene core 6 was also prepared by the Cu-mediated homo-coupling reaction of 2 in excellent yield. The FcTCBDs 7-11 connected by arylamine and azobenzene cores were synthesized in a one-step procedure consisting of formal [2 + 2] cycloaddition reaction of alkynes 2-6 with TCNE, followed by retroelectrocyclization of the initially formed cyclobutene derivatives. Intramolecular CT absorption bands were found in UV-vis spectra of the FcTCBD chromophores 7-11. Analyses by CV and DPV showed that the FcTCBDs 7-11 exhibited a reversible multi-stage reduction wave, as well as a reversible one-stage oxidation wave. Moreover, significant color changes of the FcTCBDs were observed during the electrochemical reduction. In particular, FcTCBD 8 constructed by diphenylamine spacer exhibited significant color changes, attributable to the generation of diand tetraanionic species during the electrochemical reaction.

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

General. Melting points were determined with a Yanagimoto MPS3 micromelting apparatus, and the solvent in the parenthesis shows the solvent used for recrystallization. The HRMS data were obtained with a JEOL JMS-700 instrument using 3-nitrobenzylalcohol as a matrix for FAB–MS. The IR and UV–vis spectra were recorded with JASCO FTIR-4100 and Shimadzu UV-2550 spectrophotometers. The ¹H and ¹³C NMR spectra were recorded with a JEOL ECA500 spec-

trometer at 500 and 125 MHz, respectively. The voltammetry measurements were performed with a BAS 100B/W electrochemical workstation equipped and with a standard three-electrode configuration and all measurements were carried out under an argon atmosphere. Tetraethylammonium perchlorate (0.10 M) in benzonitrile was used as a supporting electrolyte, with a platinum wire auxiliary and disk working electrodes. Reference electrode was formed from Ag/AgNO₃ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.10 M). The half-wave potential of the ferrocene/ferrocenium ion couple (Fc/Fc⁺) under these conditions using this reference electrode was confirmed by CV measurements of the couple in each sample as an internal ferrocene standard.

4-(Ferrocenvlethvnvl)aniline (2).¹¹ To a solution of 1 (466 mg, 2.22 mmol), 4-iodoaniline (725 mg, 3.31 mmol), and CuI (45 mg, 0.24 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (69 mg, 0.06 mmol). The resulting mixture was stirred at 50 °C for 22 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with CH₂Cl₂. The organic layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 2 (389 mg, 58%) as orange crystals. Mp 185.0-189.0 °C, decomp. (CH₂Cl₂), lit.: 186–188 °C;¹¹ ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.28 (d, 2H, J = 8.5 Hz, 3,5-H of C₆H₄), 6.61 (d, 2H, J = 8.5 Hz, 2,6-H of C₆H₄), 4.45 (dd, 2H, J = 1.5, 1.5 Hz, Fc, 4.22 (s, 5H, Cp), 4.19 (dd, 2H, J = 1.5, 1.5 Hz, Fc), 3.77 (br. s, 2H, NH₂).

4.4'-Bis(ferrocenvlethvnvl)diphenvlamine (3). To a solution of 1 (258 mg, 1.23 mmol), bis(4-iodophenyl)amine (210 mg, 0.50 mmol), and CuI (19 mg, 0.10 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol). The resulting mixture was stirred at 50 °C for 22 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with CH₂Cl₂. The organic layer was washed with brine, dried with Na2SO4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 to give 3 (189 mg, 65%) as orange crystals. Mp 164.0–166.0 °C (CHCl₃/EtOH); IR (ATR): $v_{max} =$ 3389 (w), 3087 (w), 2203 (w), 1599 (s), 1578 (w), 1518 (s), 1483 (w), 1459 (w), 1436 (w), 1412 (w), 1397 (w), 1378 (w), 1318 (s), 1237 (w), 1204 (w), 1182 (w), 1160 (w), 1107 (m), 1058 (w), 1029 (w), 1001 (m), 925 (m), 877 (w), 814 (s), 752 (w), 723 (w), 714 (w), 691 (w), 676 (w), 669 (w), 661 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.40 (d, 4H, J =8.7 Hz, 3,3',3''-H of C₆H₄), 7.03 (d, 4H, J = 8.7 Hz, 2,2',2''-H of C_6H_4), 4.49 (dd, 4H, J = 1.8, 1.8 Hz, Fc), 4.25 (s, 10H, Cp), 4.23 (dd, 4H, J = 1.8, 1.8 Hz, Fc); Low solubility hampered the measurement of ¹³C NMR; HRMS (FAB): calcd for C₃₆H₂₇Fe₂N⁺ [M]⁺ 585.0842; found: 585.0843.

3,6-Bis(ferrocenylethynyl)carbazole (4). To a solution of **1** (638 mg, 3.04 mmol), 3,6-diiodocarbazole (419 mg, 1.00 mmol), and CuI (38 mg, 0.20 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)-palladium(0) (68 mg, 0.06 mmol). The resulting mixture was stirred at 50 °C for 20 h under an Ar atmosphere. The reaction

mixture was poured into a 10% NH₄Cl solution and extracted with CH₂Cl₂. The organic layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 4 (560 mg, 96%) as orange crystals. Mp 220.0–221.0 °C, decomp. (CHCl₃/EtOH); IR (ATR): $\nu_{max} =$ 3394 (s), 3114 (w), 2203 (w), 1749 (w), 1618 (w), 1600 (w), 1575 (w), 1519 (w), 1494 (s), 1453 (m), 1436 (w), 1415 (w), 1389 (w), 1320 (w), 1295 (w), 1284 (m), 1238 (s), 1203 (w), 1160 (w), 1135 (w), 1106 (m), 1059 (w), 1032 (m), 1022 (m), 1006 (m), 948 (w), 923 (m), 893 (s), 846 (s), 818 (s), 810 (s), 787 (w), 775 (w), 761 (w), 752 (w), 734 (w), 722 (w), 714 (w), 707 (w), 697 (w), 671 (w), 659 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 8.22 (s, 2H, 4,5-H of Cz), 8.20 (s, 1H, NH of Cz), 7.56 (dd, 2H, J = 8.5, 1.5 Hz, 2.7-H of Cz), 7.38 (br. d. 2H, J = 8.5 Hz, 1,8-H of Cz), 4.54 (dd, 4H, J = 1.8, 1.8 Hz, Fc), 4.28 (s, 10H, Cp), 4.25 (dd, 4H, J = 1.8, 1.8 Hz, Fc); Low solubility hampered the measurement of ¹³CNMR; HRMS (FAB): calcd for C₃₆H₂₅Fe₂N⁺ [M]⁺ 583.0686; found: 583.0686.

4,4',4"-Tris(ferrocenylethynyl)triphenylamine (5).¹² To a solution of 1 (946 mg, 4.50 mmol), tris(4-iodophenyl)amine (632 mg, 1.00 mmol), and CuI (57 mg, 0.30 mmol) in triethylamine (10 mL) and THF (10 mL) was added tetrakis(triphenylphosphine)palladium(0) (90 mg, 0.08 mmol). The resulting mixture was stirred at 50 °C for 5 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with CH₂Cl₂. The organic layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 5 (828 mg, 95%) as orange crystals. Mp 158.0-161.0 °C, decomp. (CH₂Cl₂); Melting point is not shown in the literature;¹² ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.37 (d, 6H, J = 8.5 Hz, 3,3',3''-H of C₆H₄), 7.03 (d, 6H, J =8.5 Hz, 2,2',2''-H of C₆H₄), 4.48 (dd, 6H, J = 2.0, 2.0 Hz, Fc), 4.24 (s, 15H, Cp), 4.23 (dd, 6H, J = 2.0, 2.0 Hz, Fc).

4,4'-Bis(ferrocenylethynyl)azobenzene (6). To a solution of 2 (218 mg, 0.72 mmol) in toluene (10 mL) was added CuBr (10 mg, 0.07 mmol) and pyridine (31 mg, 0.39 mmol). The resulting mixture was stirred at 60 °C for 22 h under air. The reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 6 (216 mg, 99%) as red crystals. Mp 183.0-187.0 °C, decomp. (CH₂Cl₂); IR (ATR): $\nu_{max} = 3093$ (w), 2201 (m), 1594 (s), 1556 (w), 1520 (w), 1503 (m), 1457 (w), 1411 (m), 1298 (w), 1286 (w), 1227 (w), 1152 (m), 1106 (m), 1038 (m), 1019 (m), 1000 (m), 927 (m), 895 (m), 877 (w), 855 (s), 823 (s), 811 (s), 780 (w), 758 (m), 748 (m), 733 (m), 718 (m), 693 (m), 683 (m), 675 (m), 664 (w), 655 (w) cm⁻¹; UV-vis (CH_2Cl_2) : $\lambda_{max} (\log \varepsilon) = 260 (4.53), 292 \text{ sh} (4.54), 334 (4.74),$ 465 (4.55), 626 sh (3.06), 690 sh (2.49) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.89 (d, 4H, J = 8.5 Hz, 2,6,2',6'-H of C₆H₄), 7.61 (d, 4H, J = 8.5 Hz, 3,5,3',5'-H of C₆H₄), 4.55 (br. s, 4H, Fc), 4.29 (br. s, 4H, Fc), 4.28 (s, 10H, Cp); ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ 151.77 (C-1,1' of C₆H₄), 132.30 (C-3,5,3',5' of C₆H₄), 127.19 (C-4,4' of C₆H₄), 123.16 (C-2,6,2',6' of C₆H₄), 91.90 (C=C), 86.05 (C=C), 71.80 (CH of Fc), 70.25 (Cp of Fc),

69.29 (*C*H of Fc), 65.17 (*ipso-C* of Fc); HRMS (FAB): calcd for $C_{36}H_{26}Fe_2N_2^+$ [M]⁺ 598.0795; found: 598.0783.

4-(1,1,4,4-Tetracyano-2-ferrocenyl-1,3-butadien-3-yl)aniline (7). TCNE (127 mg, 0.98 mmol) was added to a solution of 2 (148 mg, 0.49 mmol) in CH₂Cl₂ (5 mL). The resulting mixture was stirred for 1h at room temperature under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 7 (136 mg, 64%) as green crystals. Mp 244.0–246.0 °C, decomp. (CH₂Cl₂/hexane); IR (ATR): $\nu_{max} =$ 3355 (m), 2960 (w), 2226 (w), 1632 (m), 1602 (s), 1518 (s), 1445 (s), 1336 (m), 1286 (s), 1213 (s), 1180 (s), 1126 (m), 1044 (m), 872 (m), 811 (s), 775 (m), 696 (m), 666 (m) cm⁻¹; UV-vis $(CH_2Cl_2): \lambda_{max} (\log \varepsilon) = 236 (4.22), 270 \text{ sh} (4.06), 354 (4.32),$ 421 (4.29), 617 (3.41) nm; UV-vis (10% CH₂Cl₂/hexane); $\lambda_{\max} (\log \varepsilon) = 234 (4.19), 262 \text{ sh} (4.07), 345 (4.33), 403 (4.28),$ 597 (3.35) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.59 (d, 2H, $J = 8.9 \text{ Hz}, 3.5 \text{-H of } C_6 \text{H}_4), 6.66 \text{ (d, 2H, } J = 8.9 \text{ Hz}, 2.6 \text{-H of }$ C₆H₄), 5.24 (m, 1H, Fc), 4.93 (m, 1H, Fc), 4.81 (m, 1H, Fc), 4.66 (m, 1H, Fc), 4.49 (br. s, 2H, NH₂), 4.44 (s, 5H, Cp); ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ 173.92 [C=C(CN)₂], 164.58 [C=C(CN)₂], 152.72 (C-4 of C₆H₄), 132.22 (C-3,5 of C₆H₄), 120.41 (C-1 of C₆H₄), 114.84 (C-2,6 of C₆H₄), 113.95 (CN), 113.54 (CN), 113.15 (CN), 112.98 (CN), 79.65 [C(CN)₂], 78.46 [C(CN)₂], 76.17 (ipso-C of Fc), 75.33 (CH of Fc), 74.75 (CH of Fc), 72.56 (Cp of Fc), 72.16 (CH of Fc), 71.95 (CH of Fc); HRMS (FAB): calcd for C₂₄H₁₅FeN₅⁺ [M]⁺ 429.0677; found: 429.0670.

4,4'-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)diphenylamine (8). TCNE (119 mg, 0.93 mmol) was added to a solution of 3 (182 mg, 0.31 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was refluxed for 22 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 8 (227 mg, 87%) as red crystals. Mp 150.0-153.0 °C (CH₂Cl₂/hexane); IR (ATR): $\nu_{max} = 3344$ (w), 2224 (m), 1590 (m), 1506 (s), 1440 (m), 1415 (w), 1383 (w), 1333 (m), 1269 (m), 1181 (s), 1110 (w), 1047 (w), 1005 (w), 937 (w), 831 (m), 774 (w), 736 (w), 700 (w), 663 (w) cm⁻¹; UV-vis (CH_2Cl_2) : $\lambda_{max} (\log \varepsilon) = 255 (4.52), 310 \text{ sh} (4.41), 353 (4.55),$ 475 (4.71), 620 (3.76) nm; UV-vis (30% CH₂Cl₂/hexane): λ_{max} $(\log \varepsilon) = 253$ (4.52), 310 sh (4.40), 349 (4.54), 461 (4.71), 610 (3.76) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.63 (d, 4H, J =8.8 Hz, 3,5,3'5'-H of C₆H₄), 7.17 (d, 4H, J = 8.8 Hz, 2,6,2',6-H of C₆H₄), 6.89 (s, 1H, NH), 5.39 (br. s, 2H, Fc), 5.02 (br. s, 2H, Fc), 4.86 (br. s, 2H, Fc), 4.55 (br. s, 2H, Fc), 4.45 (s, 10H, Cp); ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ 173.23 [C=C(CN)₂ × 2], 164.44 [C=C(CN)₂ × 2], 146.03 (C-4,4' of C₆H₄), 131.56 (C-3,5 or C-3',5' of C₆H₄), 131.48 (C-3,5 or C-3',5' of C₆H₄), 124.65 (C-1,1' of C₆H₄), 118.41 (C-2,6 or C-2',6' of C₆H₄), 118.23 (C-2,6 or C-2',6' of C₆H₄), 113.77 (CN \times 2), 113.13 $(CN \times 2)$, 112.75 $(CN \times 2)$, 112.41 $(CN \times 2)$, 82.12 $[C(CN)_2]$, 82.09 [$C(CN)_2$], 78.89 ([$C(CN)_2$] × 2), 76.19 (*ipso-C* of Fc), 75.92 (ipso-C of Fc), 75.37 (CH of Fc × 2), 75.34 (CH of Fc), 75.09 (CH of Fc), 72.85 (Cp of Fc), 72.81 (Cp of Fc), 72.61 (CH of Fc), 72.52 (CH of Fc), 71.61 (CH of Fc \times 2); HRMS (FAB): calcd for $C_{48}H_{27}Fe_2N_9^+$ [M]⁺ 841.1088; found: 841.1109.

3,6-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)carbazole (9). TCNE (193 mg, 1.51 mmol) was added to a

solution of 4 (291 mg, 0.50 mmol) in CH₂Cl₂ (10 mL). The resulting mixture was refluxed for 22 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 9 (391 mg, 93%) as green crystals. Mp 212.0–213.0 °C, decomp. (CH₂Cl₂/hexane); IR (ATR): $\nu_{max} =$ 3403 (w), 2224 (w), 1631 (w), 1602 (w), 1525 (s), 1443 (w), 1411 (w), 1380 (w), 1332 (w), 1308 (w), 1254 (m), 1188 (w), 1146 (w), 1110 (w), 1045 (w), 1004 (w), 931 (w), 897 (w), 822 (m), 771 (w), 706 (w), 659 (w) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} $(\log \varepsilon) = 286 (4.44), 306 \text{ sh} (4.43), 347 (4.44), 423 (4.32), 631$ (3.62) nm; UV–vis (30% CH₂Cl₂/hexane): λ_{max} (log ε) = 284 (4.45), 304 sh (4.42), 345 (4.43), 414 (4.32), 621 (3.55) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 8.94 (s, 1H, NH), 8.38 (d, 1H, J = 1.8 Hz, 4-H or 5-H of Cz), 8.33 (d, 1H, J = 1.8 Hz, 4-H or 5-H of Cz), 7.80 (dd, 2H, J = 7.0, 7.0 Hz, 2,7-H of Cz), 7.55 (dd, 2H, J = 7.0, 7.0 Hz, 1,8-H of Cz), 5.33 (m, 2H, Fc), 5.02 (m, 1H, Fc), 5.00 (m, 1H, Fc), 4.87 (m, 1H, Fc), 4.85 (m, 1H, Fc), 4.69 (m, 2H, Fc), 4.48 (s, 5H, Cp), 4.45 (s, 5H, Cp); Low solubility hampered the measurement of ¹³CNMR; HRMS (FAB): calcd for $C_{48}H_{25}Fe_2N_9^+$ [M]⁺ 839.0932; found: 839.0938.

4,4',4"-Tris(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)triphenylamine (10). TCNE (116 mg, 0.91 mmol) was added to a solution of 5 (174 mg, 0.20 mmol) in CH₂Cl₂ (10 mL). The resulting mixture was refluxed for 22 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give 10 (204 mg, 81%) as reddish brown crystals. Mp 203.0-205.0 °C (CH₂Cl₂/hexane); IR (ATR): $v_{\text{max}} = 3116$ (w), 2224 (w), 1591 (m), 1523 (s), 1500 (s), 1442 (m), 1414 (w), 1382 (w), 1333 (m), 1298 (m), 1267 (m), 1198 (m), 1184 (m), 1109 (w), 1094 (w), 1043 (w), 1004 (w), 931 (w), 895 (w), 828 (s), 773 (m), 760 (w), 742 (w), 703 (w), 692 (w), 679 (m), 669 (m) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} $(\log \varepsilon) = 256$ (4.58), 308 sh (4.54), 350 (4.54), 480 (4.64), 624 (3.82) nm; UV-vis (30% CH₂Cl₂/hexane): λ_{max} (log ε) = 254 (4.57), 302 (4.51), 349 (4.53), 469 (4.64), 610 (3.81) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 7.56 (br. d, 6H, J = 9.0 Hz, 3,5,3',5',3'',5''-H of C₆H₄), 7.12 (br. d, 6H, J = 9.0 Hz, 2,6,2',6',2",6"-H of C₆H₄), 5.48 (br. s, 3H, Fc), 5.06 (br. s, 3H, Fc), 4.90 (br. s, 3H, Fc), 4.49 (br. s, 3H, Fc), 4.47 (s, 15H, Cp); 13 C NMR (125 MHz, CDCl₃): δ_{C} 172.61 [C=C(CN)₂], 164.31 [C=C(CN)₂], 149.66 (C-4,4',4" of C₆H₄), 131.12 (C-3,5,3',5',3",5" of C₆H₄), 127.53 (C-1,1',1" of C₆H₄), 125.03 (C-2,6,2',6',2",6" of C₆H₄), 113.57 (CN), 113.00 (CN), 112.08 (CN), 111.90 (CN), 84.65 [C(CN)₂], 78.90 [C(CN)₂], 76.37 (CH of Fc), 75.28 (CH of Fc), 75.12 (ipso-C of Fc), 73.02 (Cp of Fc), 72.91 (CH of Fc), 71.26 (CH of Fc); HRMS (FAB): calcd for $C_{72}H_{39}Fe_3N_{13}^+$ [M]⁺ 1253.1500; found: 1253.1468.

4,4'-Bis(1,1,4,4-tetracyano-2-ferrocenyl-1,3-butadien-3-yl)azobenzene (11). TCNE (79 mg, 0.62 mmol) was added to a solution of **6** (120 mg, 0.20 mmol) in CH₂Cl₂ (10 mL). The resulting mixture was refluxed for 22 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **11** (101 mg, 59%) as dark green crystals. Mp 160.0–162.0 °C, decomp. (CH₂Cl₂/hexane); IR (ATR): $\nu_{max} = 3109$ (w), 2222 (m), 1591 (m), 1519 (s), 1444 (m), 1413 (w), 1384 (w), 1334 (m), 1269 (m), 1181 (m), 1109 (w), 1046 (w), 1006 (w), 938 (w), 896 (w), 829 (m), 772 (m), 731 (w), 700 (w), 671 (m) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} (log ε) = 257 sh (4.32), 364 (4.73), 506 sh (3.53), 615 (3.65) nm; UV-vis $(10\% \text{ CH}_2\text{Cl}_2/\text{hexane}): \lambda_{\text{max}} (\log \varepsilon) = 258 \text{ sh} (4.28), 359$ (4.71), 502 (3.54), 600 (3.62) nm; ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ 8.03 (d, 4H, $J = 8.7 \,\text{Hz}$, 2,6,2',6'-H of C₆H₄), 7.78 (d, 4H, J = 8.7 Hz, 3,5,3',5'-H of C₆H₄), 5.42 (br. s, 2H, Fc), 5.04 (br. s, 2H, Fc), 4.89 (br. s, 2H, Fc), 4.57 (br. s, 2H, Fc), 4.44 (s, 10H, Cp); ¹³C NMR (125 MHz, CDCl₃): $\delta_{\rm C}$ 172.07 $[C=C(CN)_2]$, 165.34 $[C=C(CN)_2]$, 154.69 (C-1 or C-4 of C₆H₄), 134.11 (C-1 or C-4 of C₆H₄), 130.08 (C-3,5,3',5' of C₆H₄), 124.49 (C-2,6,2',6' of C₆H₄), 113.67 (CN), 113.08 (CN), 111.54 (CN), 111.51 (CN), 87.49 [C(CN)₂], 78.77 [C(CN)₂], 76.35 (CH of Fc), 75.39 (CH of Fc), 74.72 (ipso-C of Fc), 72.94 (Cp of Fc), 72.82 (CH of Fc), 71.46 (CH of Fc); HRMS (FAB): calcd for $C_{48}H_{26}Fe_2N_{10}^+$ [M]⁺ 854.1041; found: 854.1070.

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Supporting Information

Figure of NMR, UV–vis spectra, cyclic and differential pulse voltammograms of reported compounds. This material is available electronically on J-STAGE.

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