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Multimetallic Complex Composed of Redox-Active Bridging Quinonediimine Ligand

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A π-conjugated quinonediimine ligand possessing two terminal redox-active ferrocenyl groups, *N*,*N*′-bis{(4′-ferrocenylcarboxamide)phenyl}-1,4-benzoquinonediimine (**L**$_{\mathbf{ox}}$), was synthesized. The quinonediimine ligand **L**$_{\mathbf{ox}}$ was reduced to **L**$_{\mathbf{red}}$ composed of the phenylenediamine moiety on treatment with hydrazine hydrate. The reaction of **L**$_{\mathbf{ox}}$ with the palladium(II) complex **1** bearing the *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide ligand afforded the multimetallic complex **2**. Variable temperature ^{1}H NMR studies of **2** indicated the existence of *syn* and *anti* isomers, in which the *anti* isomer is enthalpically more favorable than the *syn* isomer in CD_2Cl_2 by 0.9 kcal mol^{-1}, but entropically less favorable by 2.6 cal mol^{-1} K^{-1} from the van’t Hoff plot. The redox function of the quinonediimine moiety is modulated by complexation with **1**. The complex **2** showed three separate redox waves, which are assignable to the successive one-electron reduction of the quinonediimine moiety and oxidation of the two terminal ferrocenyl groups. Chemical reduction of **2** in CH_2Cl_2 with $[Co(Cp)_2]$ resulted in the appearance of ESR signals with weak ^{105}Pd coupling centered around $g = 2.004$. The unpaired electron appears to locate mostly on the quinonediimine moiety with some delocalization onto the palladium center.

π-Conjugated ligands attract much interest in a variety of applications depending on their electrical properties.[1] The incorporation of transition metal complexes into such π-conjugated ligands is envisaged to provide efficient redox systems. From these points of view, bimetallic complexes composed of π-conjugated bridging spacers and terminal redox-active transition metals have received much attention as functional materials.[2] Quinonediimine (qd) derivatives are present in three redox forms, which include the reduced phenylenediamine dianions, the partially reduced semiquinonediimine radical anions, and the oxidized neutral quinonediimines. Combination of this redox behavior and complexation with transition metals is considered to provide a route to an efficient redox system. In a previous paper, complexation of π-conjugated polymer ligands bearing multi-coordination sites with transition metals was demonstrated to afford multimetallic conjugated complexes.[3,4] Furthermore, the controlled complexation with the redox-active π-conjugated ligand, *N*,*N*′-bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine, as a model molecule of polyaniline, was achieved to form the conjugated polymeric complex, the conjugated trimetallic macrocycle, or the conjugated bimetallic complex depending on coordination mode.[5] One-pot preparation of the conjugated bimetallic complex could be carried out by the in-situ oxidation of 1,4-phenylenediamine.[6] We herein report the synthesis of the multimetallic complex derived from the quinonediimine ligand possessing two terminal redox-active ferrocenyl groups.

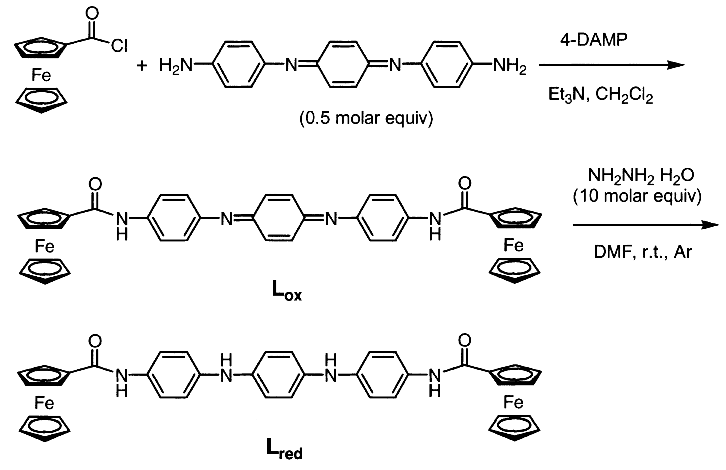
Results and Discussion

The π-conjugated quinonediimine ligand **L**$_{\mathbf{ox}}$ possessing two terminal redox-active ferrocenyl groups was synthesized from (chlorocarbonyl)ferrocene and 0.5 molar equiv of *N*,*N*′-bis(4′-aminophenyl)-1,4-benzoquinonediimine[7] (Scheme 1). The thus-obtained **L**$_{\mathbf{ox}}$ was fully characterized by spectral data and elemental analysis.

The redox properties of **L**$_{\mathbf{ox}}$ were studied chemically and electrochemically. The quinonediimine ligand **L**$_{\mathbf{ox}}$ was converted to **L**$_{\mathbf{red}}$, which is composed of the phenylenediamine moiety, by reduction with hydrazine hydrate (Scheme 1). The reduction process was monitored by UV-vis spectra (Fig. 1). The broad absorption around 496 nm, which is assignable to charge transfer from the benzenoid moiety to the quinoid moiety, gradually disappeared after the addition of 10 molar equiv of hydrazine hydrate. The formation of **L**$_{\mathbf{red}}$ was also supported by the amine NH stretching band at 3299 cm^{-1} (KBr pellet) after isolation. The electrochemical data for **L**$_{\mathbf{ox}}$ and **L**$_{\mathbf{red}}$ are shown in Table 1. The quinonediimine moiety of **L**$_{\mathbf{ox}}$ showed an irreversible two-electron reduction wave at -1.51 V vs Fc/Fc$^+$. On the other hand, **L**$_{\mathbf{red}}$ displayed two reversible one-electron redox couples at -0.10 and 0.36 V. The oxidation wave of the two terminal ferrocenyl moieties was observed at 0.18 V in cases of both **L**$_{\mathbf{ox}}$ and **L**$_{\mathbf{red}}$.

Treatment of **L**$_{\mathbf{ox}}$ with 2 molar equiv of the palladium(II) complex $[(L^1)Pd(MeCN)]$ (**1**, L^1H_2 = *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide)[7] bearing one interchangeable coordination site led to the formation of the 1:2 conjugated complex [(L^1)Pd(**L**$_{\mathbf{ox}}$)Pd(L^1)] (**2**, Scheme 2). The electronic spectrum of **2** in CH_2Cl_2 exhibited a broad absorption around 598 nm, probably assignable to a low-energy charge transfer transition with significant contribution from palladium (Fig. 2).

Variable temperature ^{1}H NMR studies of the conjugated complex **2** indicated the existence of *syn* and *anti* isomers in solution. The protons of the quinonediimine moiety of the *syn*



Scheme 1.

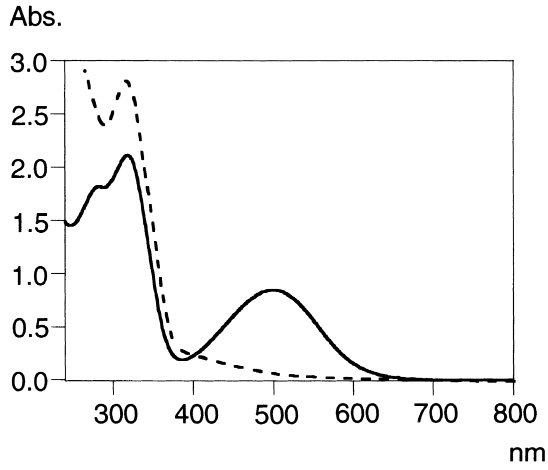


Fig. 1. Electronic spectra of $\mathbf{L}_{\mathbf{ox}}$ (—) and $\mathbf{L}_{\mathbf{red}}$ (---) (5.0×10^{-5} M) in CH_2Cl_2.

Table 1. Electrochemical Data for Ligand $\mathbf{L}_{\mathbf{ox}}$, $\mathbf{L}_{\mathbf{red}}$, and Complex **2**[a)]

$\mathbf{L}_{\mathbf{ox}}$	-1.51[b)]	—	0.18
$\mathbf{L}_{\mathbf{red}}$	-0.10	0.36	0.18
2	-1.25	-0.60	0.18

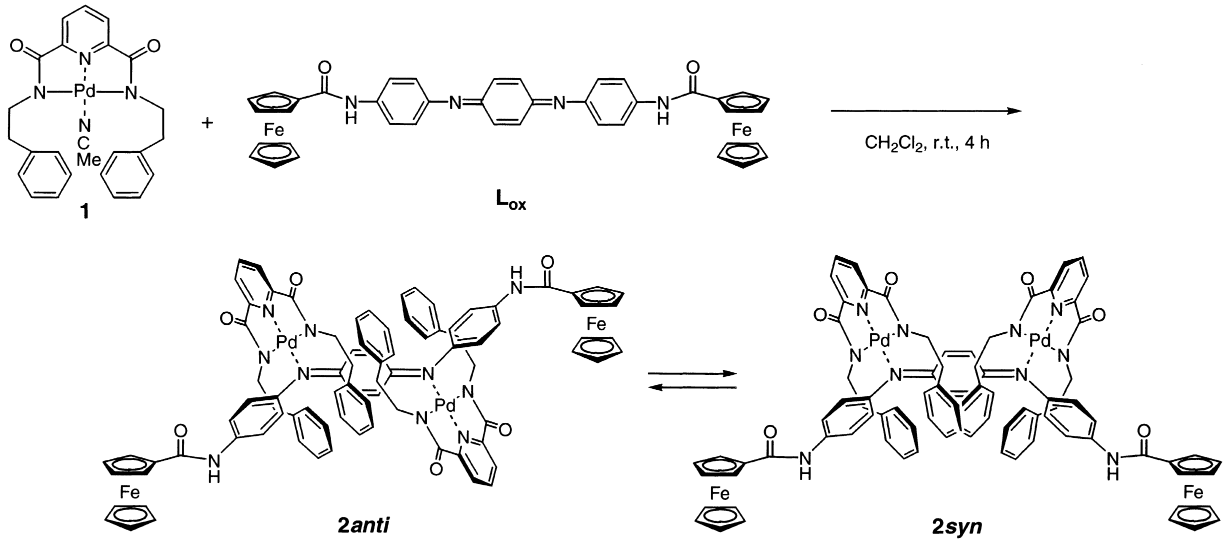
a) $E_{1/2}$(V) vs Fc/Fc$^+$; obtained in CH_2Cl_2 solution (1.0×10^{-3} M, 0.1 M Bu_4NClO_4 supporting electrolyte) with scan rate = 100 mV/s under argon. b) Irreversible reduction wave.

isomer were observed as singlet peaks. On the other hand, the *anti* isomer exhibited doublet peaks of those protons. As the temperature was lowered, the peaks of the conformer ***2anti*** increased gradually. The equilibrium constant K_{eq} between ***2syn*** and ***2anti*** was calculated from variable temperature ^{1}H NMR spectra. The temperature dependence of K_{eq} is used to construct the van't Hoff plot of ln K_{eq} vs T^{-1}. The complex ***2anti*** was revealed to be enthalpically more favorable than ***2syn*** in CD_2Cl_2 by 0.9 kcal mol^{-1}, but entropically less favorable by 2.6 cal mol^{-1} K^{-1} from the van't Hoff plot.

The electrochemical properties of **2** were studied by cyclic voltammetry. The complex **2** in CH_2Cl_2 showed three separate redox waves ($E_{1/2} = -1.25$ V, -0.60 V, and 0.18 V vs Fc/Fc$^+$) as depicted in Fig. 3. The reversible redox wave at -0.60 V and pseudoreversible redox wave at -1.25 V are assigned to the successive one-electron reduction of the quinonediimine moiety to form the corresponding reduced species, $\mathbf{2}^{\bullet-}$ and $\mathbf{2}^{-}$. This result is in sharp contrast to the above-mentioned irreversible reduction of $\mathbf{L}_{\mathbf{ox}}$ (Table 1). Generally, the generated radical anion appears to be unstable, which is known to depend on the availability of a proton source.[8] In the reduction of **2**, the added electrons are considered to be delocalized over the Pd$^{\mathrm{II}}$-quinonediimine d–π^* system. Complexation is likely to render the quinonediimine stabilized as an electron sink. Accordingly, the redox properties of the quinonediimine moiety are modulated by complexation with the palladium complex **1**. Furthermore, the pseudoreversible redox wave with doubled height at 0.18 V is attributable to two one-electron oxidation processes of the two terminal ferrocenyl groups. This oxidation wave was not shifted as compared with the free quinonediimine $\mathbf{L}_{\mathbf{ox}}$. The ferrocenyl moieties are suggested to be isolated from the conjugated system by the amide function. The schematic representation for the redox processes of **2** is depicted in Scheme 3.

The redox behavior of **2** was investigated spectroscopically to gain further insight into the redox properties. The chemical one-electron reduction of **2** was achieved by treatment with $[Co(Cp)_2]$ in CH_2Cl_2. The generated species $\mathbf{2}^{\bullet-}$ was characterized by a broad absorption around 840 nm (log $\varepsilon = 4.02$) as shown in Fig. 4. This broad absorption is assignable to a charge-transfer transition or to an internal transition with significant Pd content.

The ESR spectrum of $\mathbf{2}^{\bullet-}$ exhibited a signal centered at $g = 2.004$, accompanied by the hyperfine coupling due to two equivalent nitrogen nuclei and four equivalent protons with weak coupling of the ^{105}Pd nucleus (natural abundance 22.2%, $I = 5/2$) as shown in Fig. 5. This result indicates that the unpaired electron appears to locate mostly on the quinonediimine moiety with some delocalization onto the metal. The ESR signal could be approximately simulated by assuming the follow-



Scheme 2.

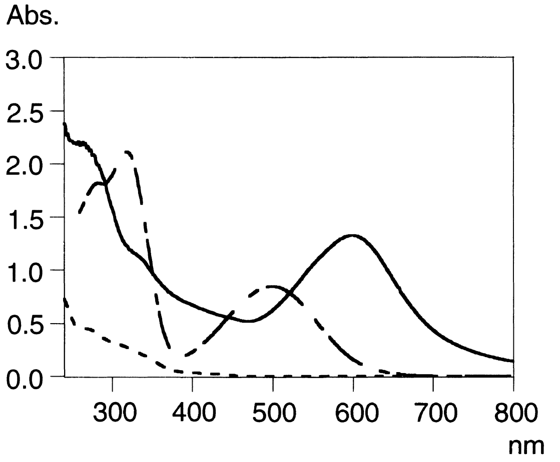


Fig. 2. Electronic spectra of $\mathbf{L}_{\mathbf{ox}}$ (– – – –), **1** (- - - -), and **2** (—) (5.0×10^{-5} M) in CH_2Cl_2.

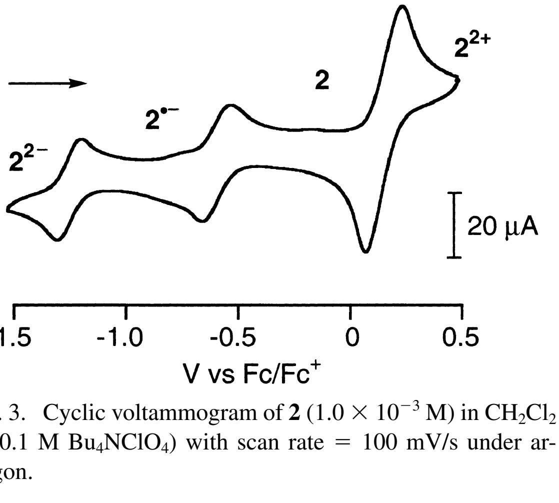
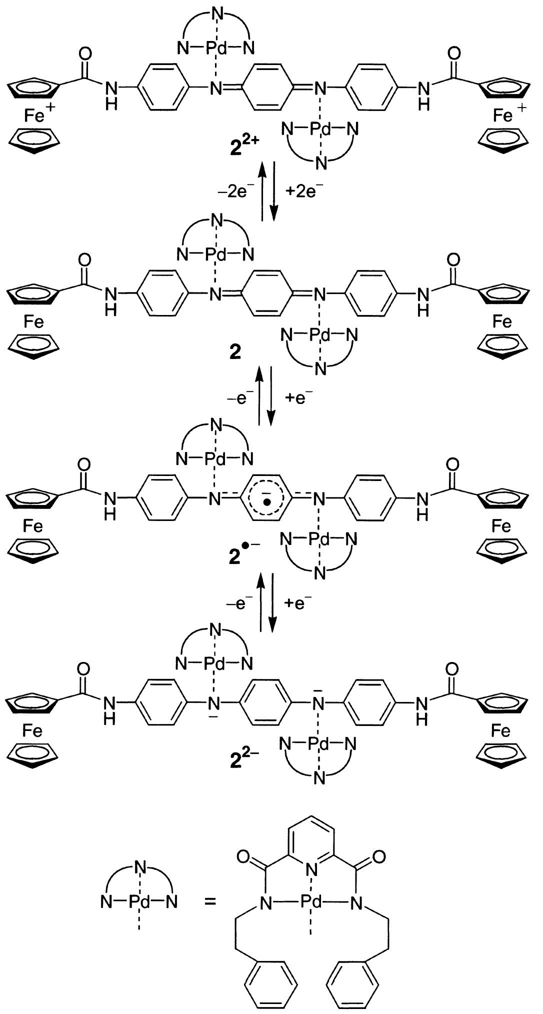


Fig. 3. Cyclic voltammogram of **2** (1.0×10^{-3} M) in CH_2Cl_2 (0.1 M Bu_4NClO_4) with scan rate = 100 mV/s under argon.



Scheme 3. Schematic representation for the redox proccesses of **2**.

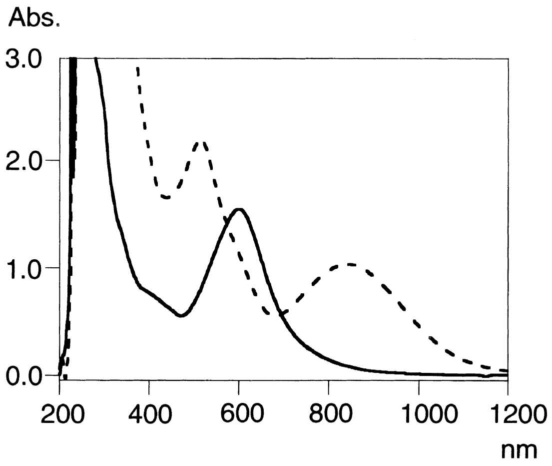


Fig. 4. Electronic spectra of **2** (—) and $\mathbf{2}^{\bullet -}$ (- -) (1.0×10^{-4} m) in CH_2Cl_2.

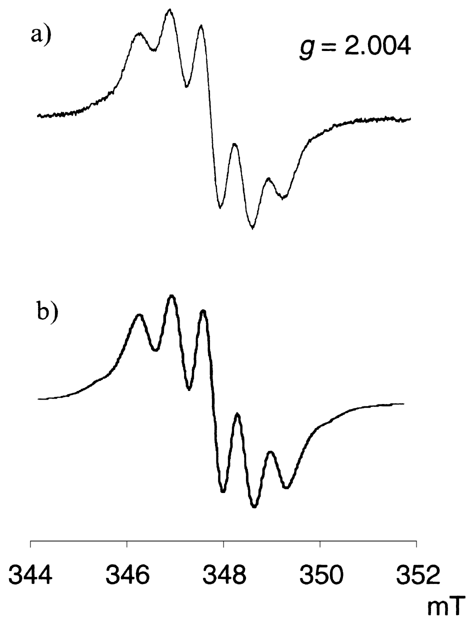


Fig. 5. a) ESR spectrum of $\mathbf{2}^{\bullet -}$ in CH_2Cl_2 at 290 K. b) The computer simulation spectrum of $\mathbf{2}^{\bullet -}$.

ing parameters: $A_N = 6.7$ G; $A_H = 1.2$ G; $A_{Pd} = 3.8$ G.

Conslusion

The π-conjugated quinonediimine ligand $\mathbf{L_{ox}}$ possessing two terminal redox-active ferrocenyl groups was synthesized and the reduction of $\mathbf{L_{ox}}$ to $\mathbf{L_{red}}$ was achieved chemically. The π-conjugated quinonediimine ligand $\mathbf{L_{ox}}$ was demonstrated to serve as a bridging ligand to afford the redox-active conjugated multimetallic complex with the palladium complex **1**. In this system, the complexed quinonediimine becomes stabilized as an electron sink. These results are related to the conjugated complexes with polyanilines.[3,4] The present conjugated multimetallic complex with the redox-active π-conjugated bridging ligand is envisaged to permit the similar potential applications as catalysts and electronic materials.

Experimental

General Comments. All reagents and solvents were purchased from commercial sources and were further purified with the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480plus. ^{1}H NMR spectra were recorded on a JEOL JNM-GSX-400 (400 MHz) spectrometer and a Varian Unity Inova 600 (600 MHz) with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. Electronic spectra were obtained by using a Hitachi U-3500 spectrophotometer. ESR spectrum was measured with Bruker ESP 300 electron spin resonance spectrophotometer. The cyclic voltammetry measurements were performed on a BAS CV-50 W voltammentry analyzer in deaerated dichloromethane containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at 298 K with a three-electrode system consisting of a stationary platinum working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/AgCl (0.01 M) reference electrode (BAS) at 100 mV/s scan rate. Potentials are given vs Fc/Fc^+.

The palladium(II) complex $[(L^1)Pd(MeCN)]$ (**1**, L^1H_2 = *N,N′*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide) was prepared according to the method reported in a previous paper.[9]

Preparation of $\mathbf{L_{ox}}$. To a stirred mixture of *N,N′*-bis(4-aminophenyl)-1,4-benzoquinonediimine (14.4 mg, 0.05 mmol), triethylamine (35 μL, 0.25 mmol) and 4-dimethylaminopyridine (1.2 mg, 0.01 mmol) in dichloromethane (2.0 mL) was dropwise added (chlorocarbonyl)ferrocene (29.7 mg, 0.12 mmol) in dichloromethane (3.0 mL) under argon at 0 °C. The mixture was stirred at 0 °C for 2 h and then stirring was continued at room temperature for 7 h. The resulting mixture was chromatographed on an alumina column with dichloromethane–ethyl acetate as an eluent to give $\mathbf{L_{ox}}$ in 68% yield. $\mathbf{L_{ox}}$: mp 266–267 °C (decomp). IR (KBr, cm^{-1}) 3252, 1643, 1585, 1501. UV-vis (CH_2Cl_2) λ_{max}/nm (log ε) 496 (4.10). ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K, *syn*:*anti* = 1:1.2) δ 7.65 (d, 4H, J = 9.0 Hz, *anti*), 7.62 (d, 4H, J = 9.0 Hz, *syn*), 7.48 (s, 2H, *anti*), 7.46 (s, 2H, *syn*), 7.09 (s, 2H, *syn*), 7.01 (d, 2H, J = 10.2 Hz, *anti*), 6.98 (d, 2H, J = 10.2 Hz, *anti*), 6.95 (d, 4H, J = 9.0 Hz, *anti*), 6.92 (d, 4H, J = 9.0 Hz, *syn*), 6.87 (s, 2H, *syn*), 4.79 (t, 4H, J = 1.8 Hz, *anti*), 4.77 (t, 4H, J = 1.8 Hz, *syn*), 4.46 (t, 4H, J = 1.8 Hz, *anti*), 4.45 (t, 4H, J = 1.8 Hz, *syn*), 4.28 (s, 10H, *anti*), 4.26 (s, 10H, *syn*). MS (FAB) *m/z* 714 (M^+ + 2). Anal. Calcd For $C_{40}H_{32}O_2N_4Fe_2$: C, 67.44; H, 4.53; N, 7.86%. Found: C, 67.35; H, 4.61; N, 7.56%.

Preparation of $\mathbf{L_{red}}$. To a DMF (5 mL) solution of $\mathbf{L_{ox}}$ (35.6 mg, 0.05 mmol) was dropwise added hydrazine hydrate (25 μL, 0.50 mmol) under argon at room temperature. The mixture was stirred at room temperature for 48 h. After evaporation of this solution, the resulting mixture was chromatographed on a silica-gel column with DMF as an eluent to give $\mathbf{L_{red}}$ in 82% yield. $\mathbf{L_{red}}$: mp 215–218 °C (decomp). IR (KBr, cm^{-1}) 3299, 1667, 1633, 1504. ^{1}H NMR (600 MHz, DMF-d_7, 298 K) δ 9.53 (s, 2H), 7.93 (s, 2H), 7.80 (d, 4H, J = 9.0 Hz), 7.24 (s, 4H), 7.19 (d, 4H, J = 9.0 Hz), 5.19 (t, 4H, J = 1.8 Hz), 4.57 (t, 4H, J = 1.8 Hz), 4.39 (s, 10H). MS (FAB) *m/z* 714 (M^+). Anal. Calcd For $C_{40}H_{34}O_2N_4Fe_2$: C, 67.25; H, 4.80; N, 7.84%. Found: C, 66.87; H, 4.81; N, 7.83%.

Preparation of Complex 2. A mixture of **1** (10.4 mg, 0.02 mmol) and ligand $\mathbf{L}_{\mathbf{ox}}$ (7.2 mg, 0.01 mmol) was stirred in dichloromethane (20 mL) under argon at room temperature for 4 h. After evaporation of this solution, the conjugated palladium complex **2** was isolated in 80% yield as dark blue powder by reprecipitation from chloroform/hexane. **2**: mp 260–261 °C (decomp). IR (KBr, cm^{-1}) 3300, 1584, 1504. UV-vis (CH_2Cl_2) λ_{max}/nm (log ε) 598 (4.50). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, *syn*:*anti* = 1:1.3) δ 9.15 (s, 2H, *syn*), 8.84 (dd, 2H, J = 10.2, 2.2 Hz, *anti*), 8.37 (s, 2H, *syn*), 8.24 (s, 2H, *anti*), 8.07 (t, 2H, J = 8.0 Hz, *anti*), 8.05 (t, 2H, J = 8.0 Hz, *syn*), 7.87 (d, 4H, J = 9.2 Hz, *syn*), 7.85 (d, 4H, J = 8.8 Hz, *anti*), 7.79 (d, 4H, J = 8.0 Hz, *anti*), 7.76 (d, 4H, J = 8.0 Hz, *syn*), 7.69 (d, 4H, J = 8.8 Hz, *anti*), 7.61 (d, 4H, J = 9.2 Hz, *syn*), 7.51 (dd, 2H, J = 10.2, 2.2 Hz, *anti*), 7.22 (s, 2H, *syn*), 7.03–6.92 (m, 24H, *syn* and *anti*), 6.84–6.82 (m, 8H, *syn*), 6.78 (d, 8H, J = 7.0 Hz, *anti*), 4.95 (t, 4H, J = 1.8 Hz, *syn*), 4.90 (t, 4H, J = 1.8 Hz, *anti*), 4.50 (t, 4H, J = 1.8 Hz, *syn*), 4.47 (t, 4H, J = 1.8 Hz, *anti*), 4.27 (s, 10H, *syn*), 4.24 (s, 10H, *anti*), 3.26–3.14 (m, 8H, *syn* and *anti*), 2.95–2.88 (m, 8H, *syn* and *anti*), 2.65–2.51 (m, 8H, *syn* and *anti*), 2.47–2.36 (m, 8H, *syn* and *anti*). MS (FAB) *m/z* 1668 (M^+). Anal. Calcd for $C_{172}H_{148}O_{12}N_{20}Fe_4Pd_4\cdot 2CHCl_3$: C, 58.46; H, 4.23; N, 7.84%. Found: C, 58.24; H, 4.38; N, 7.88%.

Generation of $\mathbf{2}^{\bullet -}$. For spectroscopic purposes, $\mathbf{2}^{\bullet -}$ was generated by treatment of **2** with 1.0 equiv of cobaltocene in dichloromethane. The cobaltocene and cobaltocenium ion presented in the reaction mixture did not significantly interfere with the electronic spectrum because of their low extinction coefficient below 400 nm.

Equilibrium Measurement for 2. Measurement of the equilibrium constants at various temperatures was carried out by integration of the appropriate peaks during ^{1}H NMR spectroscopy. Spectra were taken in CD_2Cl_2 from 243 to 298 K. The thermodynamic parameters were determined from the van't Hoff plot of ln K_{eq} vs T^{-1}.

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