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Synthesis and characterization of ferrocenylgalvinol, a novel d–π redox system

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Abstract

A novel d–π redox molecule bearing ferrocene (Fc) and galvinoxyl (GalO) units as reversible redox active sites has been synthesized and characterized. The molecule shows solvatochromic behavior and changes from a red color in *n*-hexane ($\lambda_{max} = 388$, 541 nm) to a greenish brown ($\lambda_{max} = 413$, 582 nm) in MeOH. A cyclic voltammogram of **1** under neutral conditions shows a redox process corresponding to $Fc/Fc^{\cdot+}$ but not one for GalOH (or $GalO^-$)/$GalO^{\cdot}$. Under basic conditions the latter process was observed and it occurred at a lower oxidative potential ($E^1_{1/2} = -0.074$ V vs Ag/AgCl) than the former process ($E^2_{1/2} = 0.498$ V). Thus **1** shows potential as a bilateral multi-redox molecule with pH dependence. Chemical oxidation of **1** under basic conditions (aq KOH, $K_3Fe(CN)_6$) gives an EPR spectrum with an hfc of 1.2 G attributable to Fc–$GalO^{\cdot}$.

Keywords: Radical; Ferrocene; Galvinoxyl; Solvatochromism; Redox; EPR

Functional molecules that can change their properties in response to external signaling mediated through electrons, photons, other molecules, or through heating have been the focus of considerable attention in materials science.[1] Molecules that bear multiple redox systems offer several spin-states for stepwise 1-electron oxidation/reduction, and are candidates for functional magnetic materials.[2] To date, such redox-active spin-diverse systems have mainly been prepared from transition metal complexes. Other molecules such as hetero-spin organic molecules[3] and d–π hybrid-spin molecules[4] might be useful in the construction of such multi-spin systems that exhibit multiple stepwise oxidations/reductions. Currently, there has been a limited study of such systems.

Herein, we report on a new redox molecule **1** that is composed of ferrocene (Fc) and galvinol (GalOH)[5] units as redox-active sites. The redox sites of molecule **1** therefore originate from d- and π-orbitals.

The preparation of ferrocenylgalvinol is outlined in Scheme 1. The treatment of methyl ferrocenecarboxylic acid with 2,6-di-*tert*-butyl-4-lithio-1-trimethylsilyloxybenzene in hexane at −5 °C followed by aqueous workup (NH_4Cl) gave O-silylated ferrocenyldiarylcarbinol **2** (yellow). Stepwise desilylation with AcOH and then with tetrabutylammonium fluoride in THF–MeOH afforded ferrocenylgalvinol **1**. The product was purified using silica gel chromatography to give an yield of 72%. Recrystallization from ethanol gave **1** as blackish brown needles, mp 194.0–194.5 °C.[6]

^{1}H NMR spectroscopy of **1** showed that the proton signals corresponding to the quinine moiety occur at very different chemical shifts (δ 8.21 and 6.76). NOESY experiments indicated that the former proton lies near a proton from the cyclopentadienyl ring attached to the galvinoxyl moiety. These results are consistent with the structure calculated using density functional theory simulations, as described later (Fig. 5a).

The UV–vis spectrum of ferrocenylgalvinol **1** in *n*-hexane has two bands at 388 and 541 nm, giving the solution a red color. The use of different solvents revealed

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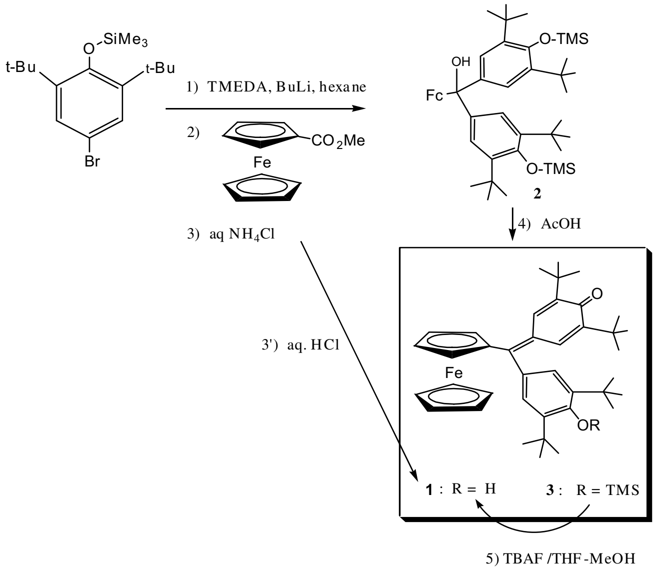


Scheme 1.

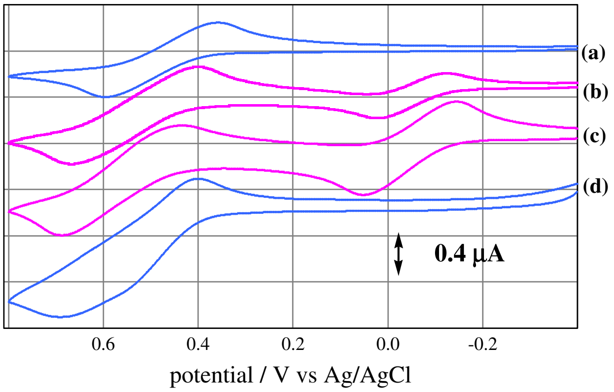


Fig. 2. Cyclic voltammograms of **1** (1.2 mM in CH_3CN containing 1.3 mM of Bu_4NBF_4 measured at a scan rate of 0.1 V s^{-1} at 25 °C using a three-electrode system (Ag/AgCl-satd-KCl, reference electrode; Pt, working and counter electrodes; the ferrocene/ferricinium wave occurs at a potential of 0.315 V vs Ag/AgCl using our equipment). Voltammograms were measured under the following conditions: (a) without the addition of any bases or acids; with the addition of (b) 0.3 equiv or (c) 0.6 equiv of Bu_4NOH in MeOH; and (d) with the addition of 1.5 equiv of CF_3CO_2H.

solvatochromic behavior;[7] the CH_2Cl_2 solution was reddish brown, whereas the MeOH solution was greenish-brown (Fig. 1). The absorption band at a longer wavelength changes more with the solvent than at a shorter wavelength band, and is not observed in either of the component molecules, galvinol or ferrocene. These results suggest that the band derives from an intramolecular CT transition between the Fc (donor) and quinone (acceptor) moieties.[8] Thus intramolecular communication between the d- and π-orbitals in **1** should be possible as designed.

In alkaline conditions, the solution of **1** turned blue. The blue color is attributable to the O-anion **4**, and was also apparent when the O-silylated derivative **3** was treated with tetrabutylammonium fluoride in CH_2Cl_2.

Cyclic voltammograms were acquired for **1** in the presence and absence of a base (Bu_4NOH) or an acid (CF_3CO_2H) (Fig. 2). Under neutral or acidic conditions, a one-electron oxidation/reduction process was observed for the ferrocenyl moiety (Fc) in **1** at +0.474 V (vs Ag/AgCl); however, no peak was observed for the redox process of GalOH (or GalO$^-$/GalO$^\bullet$). Under basic conditions (0.3 equiv Bu_4NOH), two redox couples corresponding to Fc/Fc0$^+$ and GalO$^-$ /GalO$^\bullet$ were observed at $E^1_{1/2} = -0.074$ and $E^2_{1/2} = 0.498$ V (vs Ag/AgCl), respectively (Fig. 2b). The second wave has a slightly higher potential than that observed for ferrocene itself (0.315 V), indicating that the two redox sites in **1**, Fc and GalO, interact with each other. The second oxidation process may occur at a higher oxidation potential as a result of the electron-withdrawing influence of the firstly oxidized site (GalO$^\bullet$). Thus, depending on the pH, we can obtain **5**, **6**, or **7** selectively (Scheme 2).

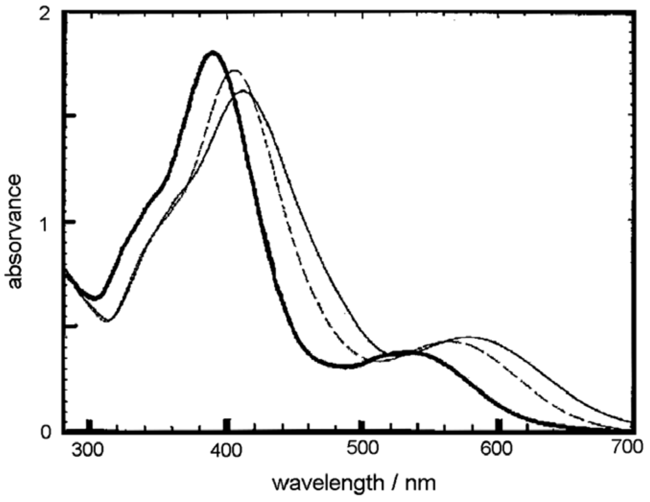
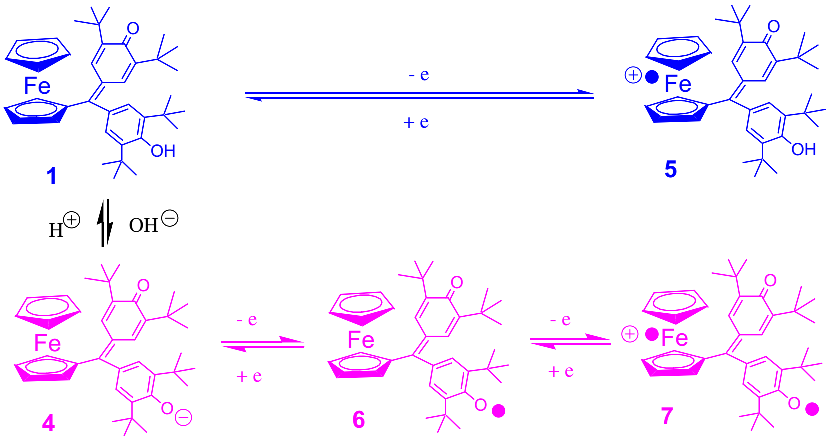


Fig. 1. The UV–vis spectrum of **1** (60 μM) in various solvents: n-hexane (thick solid line), CH_2Cl_2 (dashed line), and MeOH (thin solid line).

The chemical oxidation of **1** in benzene under basic conditions (aq KOH and $K_3Fe(CN)_6$, 1 min) gave a reddish purple solution with an absorption maximum at 513 nm (Fig. 3). The reddish purple species is considered to be due to the ferrocenylgalvinoxyl radical **6**. The phenyl-galvinoxyl-O-anion, the -O-radical, and the neutral OH derivative, in which the Fc ring in **1** is replaced with a phenyl ring, have absorption maxima in benzene at 610, 470, and 410 nm, respectively. Anion **4** and the neutral species **1** had absorption maxima in benzene at 654 and 402 nm, respectively. Thus the absorption maxima follow the series of O-anion **4** > O-radical **6** > OH derivative **1**, which fits well with the results for the phenyl derivatives. An EPR spectrum of the reddish purple solution is shown in Figure 4. The five lines of the EPR spectrum taken under a field of 1.2 G show a hyperfine coupling constant of $g = 2.003$, indicating that the unpaired electron is coupled with 4 equiv hydrogen atoms, which is similar to the behavior observed in other galvinoxy radicals in solution.[9] The equivalency arises either from roughly equal spin populations on the quinone and phenoxy rings in **6**, as discussed



Scheme 2.

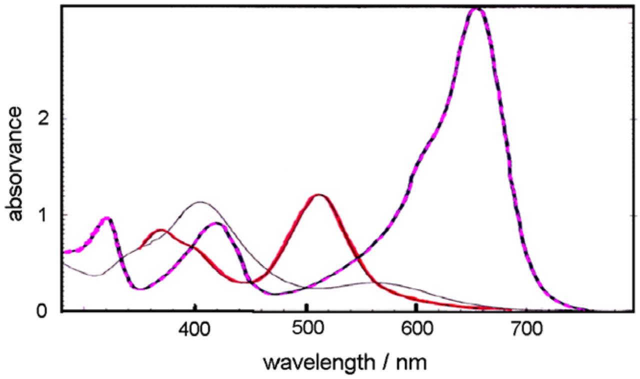


Fig. 3. The UV–vis spectra of O-anion **4** (dashed line), and O-radical **6** (red line), which was obtained by the chemical oxidation of **1** (black line).

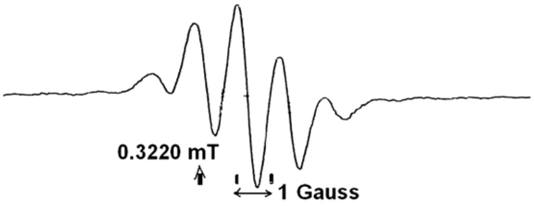


Fig. 4. The EPR spectrum of **6** obtained by chemical oxidation. The sample was the same as that used for the UV–vis spectroscopic experiment shown in Figure 3, and was degassed by evacuation and bubbling with Ar gas. Conditions: frequency = 9.03227 GHz, power = 0.06 mW, and field modulation = 0.01 mT.

later, or from a rapid flip–flop motion of these rings. Thus the reddish purple solution is attributable to monoradical **6**.

Density functional theory (DFT) calculations for some model species corresponding to **5**, **6**, and **7**, in which the *t*-butyl groups are omitted to reduce calculation costs, were performed at the U-B3LYP level with a 6-31+G* basis set for C-, H-, and O-atoms using a LanL2DZ basis set for Fe-atom. The results are visualized in Figure 5. As indicated in Figure 5b, the spin populations of **5**, which bears a ferricinium group, are localized mainly on the Fe-atom (α-spin), and partly on the Cp-rings (β-spin). In **6** (Fig. 5c), the α- and β-spin populations are delocalized on either of the galvinoxy moieties. The C-atom at the *ipso*-position in the Cp-ring has a small α-population. The small hyperfine coupling constant observed in **6** arising from the 4 H-atoms is reasonable because these H-atoms, which are attached to carbon atoms, have β-spin. The *ipso*-carbon-atom in the Cp-ring has α-spin. This spin arrangement suggests that **7** may have a singlet ground state, because such a state would not disturb the spin distribution in **5** and **6**. In fact, the DFT calculations suggest that the open-shell singlet state lies below the triplet state by 1.6 kJ/mol in **7** (Fig. 5d).

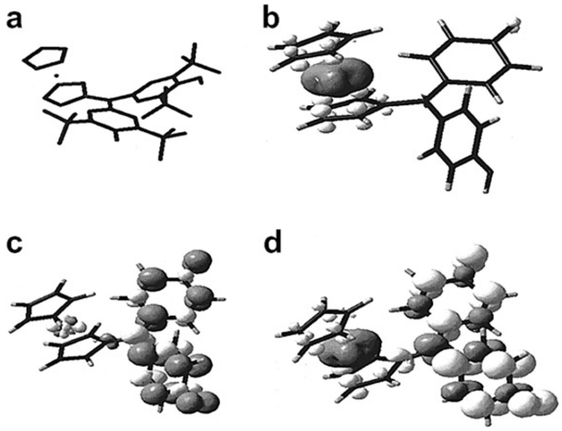


Fig. 5. The optimized structure for **1** (a) (hydrogen atoms except OH are omitted for clarity), and spin populations of model molecules for **5** (b), **6** (c), and **7** (d). The *t*-butyl groups are omitted in these model molecules during calculations. The spin maps are obtained with surfaces having a spin density of 0.003 spin/au^3 at the U-B3LYP/6-31+G*-LanL2DZ level of DFT calculations. Black and white surfaces indicate α- and β-spin, respectively.

In conclusion, the target molecule **1** (Fc–GalOH) could be converted to Fc–GalO$^-$ **4** and Fc–GalO$^\bullet$ **6** by chemical treatment. Electrochemical analysis of **1** indicates that the selective conversion of **1** to Fc$^{\bullet+}$–GalOH **5** and Fc$^{\bullet+}$–GalO$^\bullet$ **7** is possible by the change of pH. These findings will be of use for designing functional multi-redox molecules.

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6. Compound **1**: mp 194.0–194.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.21 (d, $J = 2.70$ Hz, 2H), 7.02 (s, 2H), 6.76 (d, $J = 2.70$ Hz, 2H), 5.36 (s, 1H), 4.57 (t, $J = 1.95$ Hz, 2H), 4.48 (t, $J = 1.95$ Hz, 2H), 4.18 (s, 5H), 1.47 (s, 18H), 1.45 (s, 9H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 186.29 (CO), 159.76, 153.89, 146.26, 144.66, 134.93, 133.40, 132.26, 130.08, 127.75, 127.31, 83.33, 73.57, 71.39, 70.15 (C_5H_5), 35.71, 35.08, 34.43, 30.46, 29.93, 29.44; UV (hexane) $\lambda_{max} = 388$ nm ($\log\varepsilon = 4.48$), 541 nm (3.78); (benzene) 403 nm (4.47), 550 nm (3.83); (CH_2Cl_2) 408 nm (4.47), 564 nm (3.84); (DMSO) 410 nm (4.44), 579 nm (3.84); (MeOH) 413 nm (4.43), 582 nm (3.89); IR (KBr disk, cm^{-1}) 3622, 2952, 1736, 1604.
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