



Short communication

Magnetically-enhanced electron transfer from immobilized galvinoxyl radicals

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ABSTRACT

The stability and magnetic susceptibility of galvinoxyl radicals are believed to underpin the behaviour of ferromagnetic organic layers. However, the magnetic response associated with electron transfer from galvinoxyl radicals remains little understood. Here, new findings on magnetically-enhanced electron transfer (MEET) from immobilized galvinoxyl radicals are reported in an electrochemical study using galvinoxyl–gold electrodes. The electron transfer rate constant increases by about 78% in the presence of an external magnetic field of 1.32 mT compared to the electron transfer rate in the absence of a magnetic field. The MEET of organic radical layers on a solid electrode may also open up new avenues for the development of novel ferromagnetic nanostructures and devices.

1. Introduction

Some rare organic free radicals are stable and persistent under ambient conditions: examples include diphenyl picryl hydrazyl, picryl-amino-carbazyl, and diphenyl nitrogen oxides [1,2]. The remarkable inertness toward oxygen of galvinoxyl is due to the strong kinetic protection of the unsaturated oxygen atoms provided by the vicinal *tert*-butyl substituents and the efficient delocalization of the unpaired electrons through the extensive π network [3]. More interestingly, owing to an unpaired electron, galvinoxyl, azagalvinoxyl, and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine operate as ferromagnetic phases at room temperature, which has inspired the study of ferromagnetic layers composed of radicals [4,5]. Since the organic molecular magnets are comparably small and chemically easy to control, ferromagnetic organic layers are, in some respects, superior to conventional magnets [6], especially for assembling ferromagnetic nanostructures. In the case of galvinoxyl, electron paramagnetic resonance (EPR) measurements of crystalline galvinoxyl layers, verified by scanning tunneling microscopy (STM), revealed that a so-called ferromagnetic phase exists above 85 K [7]. Dimer formation along the *c*-axis of the crystal accompanied by spin pairing has been used to explain the change in magnetism [8]. A combination of EPR and STM was used to determine the electron spin signals of galvinoxyl by applying microwaves and a magnetic field [9]. Over the past decade, theoretical studies have been carried out on crystalline galvinoxyl to understand the electron spin

exchange interactions between the unpaired electrons, the spin population, the spin arrangement and the spontaneous magnetic moment of the molecule [10–13]. Experimentally, galvinoxyl has been considered as a spin-doping candidate to enhance spin-spin interactions and manipulate spin ensembles [12,14,15]. It would be of significance to explore the spin-coupled electron transfer from galvinoxyl radicals to a solid electrode, because electron transfer in an organic–metallic device will potentially stimulate the development of novel, low-power, ultra-scaled molecular electronics (junctions, switches, transistors, spintronics, etc.) [16,17].

For a well-defined donor–acceptor system, redox-active radicals can be used to probe the electron transfer kinetics using cyclic voltammetry in both diffusion and immobilization situations [18–20]. In the case of radicals immobilized on the electrode surface, the rate of electron transfer between a donor and an acceptor is dependent on the Gibbs free energy, reorganization energy, temperature, and electronic coupling [21]. To increase the electron transfer rate, surface (electrode) modification based on self-assembled monolayers (SAMs) has been used, focusing on shortening the donor–acceptor bridge, controlling double-layer effects and eliminating diffusive mass transport, which require either replacement of materials or system modification [22]. Recently, the influence of an external magnetic field on metal oxides (Fe_3O_4 , MnO_2 , and Co_3O_4) has attracted some attention due to the effects of the Lorentz force on moving charges/ions, and spin/spin–orbit coupling-induced magnetic moments [23–25]. While galvinoxyl is itself

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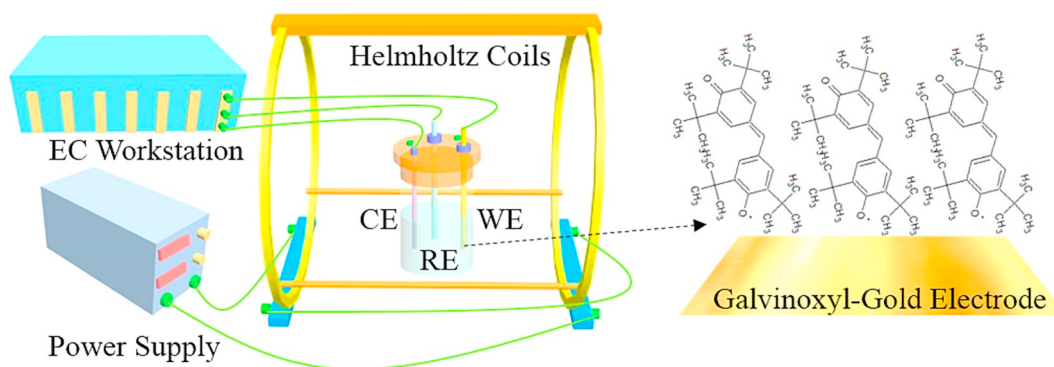


Fig. 1. A schematic view of the setup used for the electrochemical study of the galvinoxyl–gold electrode system with a magnetic field provided by Helmholtz coils.

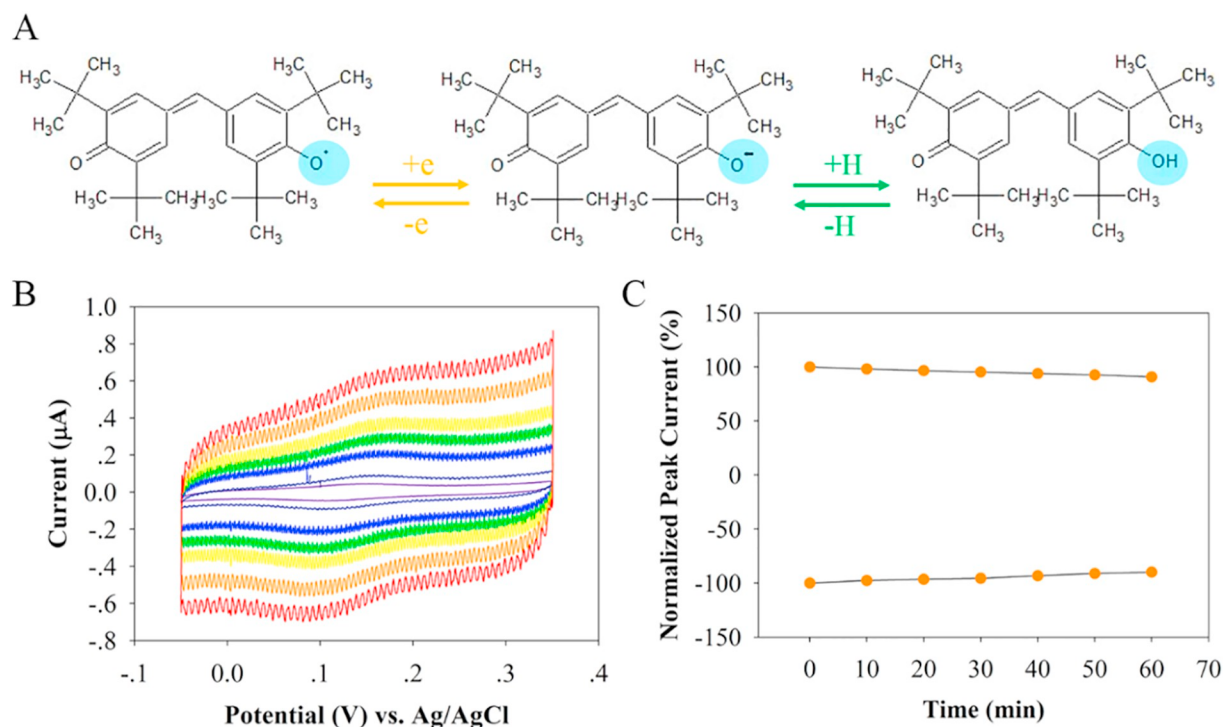


Fig. 2. (A) The scheme for a one-electron one-proton process. (B) Cyclic voltammograms for the gold electrode coated with galvinoxyl radicals in the absence of a magnetic field. Note that the scan rates are 20 mV s^{-1} , 50 mV s^{-1} , 100 mV s^{-1} , 150 mV s^{-1} , 200 mV s^{-1} , 300 mV s^{-1} , and 400 mV s^{-1} . (C) Time profiles for the peak current stability at a scan rate of 50 mV s^{-1} in the absence of a magnetic field (very reproducible, and the error bar is small).

affected by a magnetic field, little is known about how an external magnetic field affects its electron transfer kinetics as a redox active species. Herein, we report on results obtained by a cyclic voltammetry analysis of the effects of a magnetic field on the electron transfer kinetics of immobilized galvinoxyl molecules on a gold electrode.

2. Experimental

Cyclic voltammetry on immobilized galvinoxyl radicals was carried out using a Bio-Logic VMP3 electrochemical workstation with a three-electrode (Fisher Scientific) testing system (a platinum wire counter electrode, an Ag/AgCl reference electrode, and a gold working electrode (2 mm diameter) with surface area of $\sim 3.14 \text{ mm}^2$). The galvinoxyl–gold electrode system was prepared by exposing a freshly cleaned gold electrode to 500 nM galvinoxyl (Sigma-Aldrich) in absolute ethanol (ACROS Organics) for 1 h. Prior to this, the gold electrode was polished with 0.05 μm Alpha alumina powder for 5 min and cleaned thoroughly [26]. The cyclic voltammetry measurements were performed using 0.1 M Na_2HPO_4 (99.5%, Sigma-Aldrich) as the

electrolyte. A pair of Helmholtz coils in parallel was used to generate a magnetic field (Fig. 1). The setup has been described in more detail elsewhere [24]. A maximum of 1.32 mT can be obtained using this arrangement and temperature changes in the electrochemical cells due to the magnetic field are negligible [27].

3. Results and discussion

Representative voltammograms for adsorbed galvinoxyl monolayers at different scan rates are shown in Fig. 2. Both anodic and cathodic peaks are present in the cyclic voltammograms of the galvinoxyl-coated gold electrode (Fig. 2B). At pH 7.6, the formal potential at about 130 mV vs. Ag/AgCl electrode agrees with the Nernstian dependence reported elsewhere [7,18]. The full width at half-width of the redox peak gives a value of about 90 mV, corresponding to a one-electron process for the immobilized redox reaction [26]. At a pH between the neutral pH and the pH of acid dissociation, the dominant path of electron transfer couples with a one-proton process [19], which is expressed as galvinoxyl-deprotonated galvinol–galvinol (see Fig. 2A).

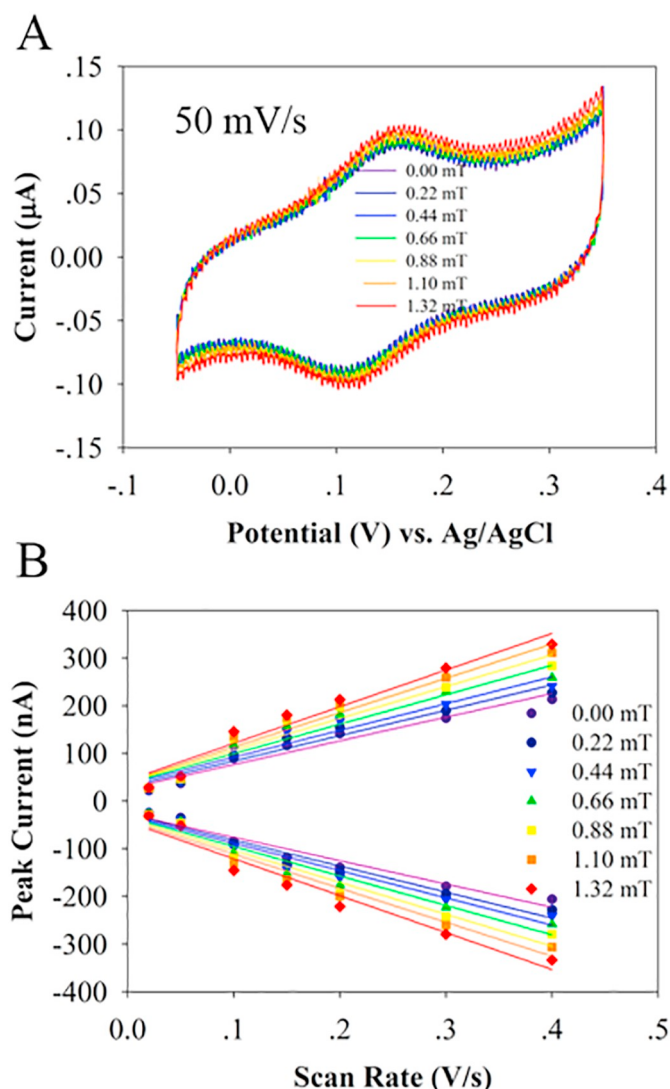


Fig. 3. (A) Cyclic voltammograms for the gold electrode coated with galvinoxyl radicals at a scan rate of 50 mV s^{-1} under different magnetic fields. (B) The linear dependence of the peak current on the voltage scan rate under different magnetic fields.

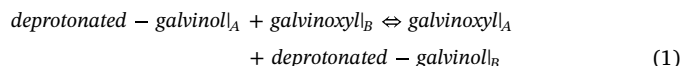
The strength of association and the stability of the adsorbed galvinoxyl radicals were assessed by monitoring the peak current. In this procedure, the gold electrode coated with galvinoxyl was placed in the solution, and after 30 s, a voltammogram was initiated with a scan rate of 50 mV s^{-1} . Fig. 2C shows a profile of the peak current as a function of time. After 60 min, $90.8 \pm 0.7\%$ (anodic) and $89.9 \pm 0.8\%$ (cathodic) of the initial peak current were maintained, indicating the good stability of the immobilized galvinoxyl on the gold electrode surface (the peak current is proportional to the amount of galvinoxyl molecules adsorbed on the gold surface).

The peak current was also measured as a function of the voltage scan rate for the stabilized electrodes coated with galvinoxyl molecules under different magnetic fields, and was found to exhibit a linear dependence on the magnetic field strength (Fig. 3). To verify the effect of a magnetic field on galvinoxyl radicals, two groups of control experiments were conducted. For the gold electrode without a galvinoxyl coating, there is no measurable difference under different magnetic fields. For gold electrodes coated with a known diamagnetic radical molecule, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH·) [28,29], there is no detectable enhancement in cyclic voltammetry under different magnetic fields. One can conclude that the difference between the CVs

at the same scan rate for the galvinoxyl–gold electrode (Fig. 3A) is a result of the effect of the magnetic field on the galvinoxyl molecules. The peak potential shifts (anodic: left-shift and cathodic: right-shift in Fig. 3A) and the slope of the peak current plotted against scan rate increases (Fig. 3B) with an increase in the magnetic field, indicating magnetically-enhanced electron transfer (MEET) [25]. Note that for the galvinoxyl–gold electrode system, the slope of the peak current versus scan rate plot (purple line in Fig. 3B), with $n = 1$, gives an active galvinoxyl molecule number of $\sim 3.18 \times 10^{11}$ ($\sim 1.68 \times 10^{-11} \text{ mol/cm}^2$) at the electrode.

The electron transfer between the galvinoxyl molecules and an electrode can be understood by assuming that the direct superexchange reaction is the dominant pathway [30–33]. The dependence of the redox peak's position on the voltage scan rate can be used to characterize the electron transfer rate constant [26]. This method was used to determine the heterogeneous electron transfer rate constants for galvinoxyl immobilized on the gold electrode. Fig. 4A shows a plot of the peak potential shift from the apparent formal potential versus the voltage scan rate for different magnetic fields. Table 1 shows the simulation results along with the best fit for the electron transfer rate constant obtained using the extended Marcus model for reorganization energy (λ) values of 0.05, 0.10, and 0.20 eV, together with the results obtained by the Laviron method [34]. Note that the electron transfer reorganization energies of isolated organic molecules are reported to be in the range 0.05–0.20 eV [35]. With a reorganization energy of 0.10 eV, in the absence of an external magnetic field, the standard heterogeneous rate constant (k) for the galvinoxyl–gold electrode system is calculated to be about 1.05 s^{-1} . In the presence of an external magnetic field, the standard rate constant was found to be 1.13, 1.26, 1.35, 1.46, 1.66, 1.87 s^{-1} for magnetic fields of 0.22, 0.44, 0.66, 0.88, 1.10, 1.32 mT (Table 1), an increase of about 8%, 20%, 29%, 39%, 58%, 78%, respectively, compared to the value without a magnetic field. A more significant change in the CVs was observed with a higher magnetic field of $\sim 100 \text{ mT}$ using N/S magnets, giving an electron transfer rate constant of $4.61 \pm 0.35 \text{ s}^{-1}$.

For the immobilized species, a system of galvinoxyl–deprotonated galvinoxyl will be present. One has a single unpaired electron and the other is diamagnetic, and two states are possible, including a doublet (D) and a singlet (S). During the electron transfer between immobilized species and gold electrode, the positions (denoted as A and B) of galvinoxyl–deprotonated galvinoxyl associated with their electronic states will change according to the following equations:



Since the singlet (deprotonated galvinoxyl) and polarized radical (galvinoxyl) form a cage complex, the degree of electron nuclear spin polarization will change under different magnetic fields. In the presence of a magnetic field, a cage with localized spin could slightly elevate the free energy of activation (Fig. 4B).

In the presence of magnetic fields, the increase in the Zeeman effect, $g\beta H$ [29], relative to the reactant energy in the absence of an applied field, contributes to the activation energy by reducing the net enthalpy of the activation barrier and thus the reaction is facilitated (Fig. 4B). One may consider that the magnetically-induced energy is too small to have a significant effect. It is plausible that when the electron Fermi level at an electrode with an external electrical field is close to the electrochemical barrier of an electron transfer reaction where a quasi-stable state is obtained, a tiny energy perturbation may facilitate the electron-transfer process. In the case of galvinoxyl radicals with an electron spin $S = 1/2$, the energy difference between the two Zeeman states is given by $E(m_s = +1/2) - E(m_s = -1/2) = g\beta H$. The small Zeeman effect may cause a significant change in the electron transfer rate reaction. Similarly, a theoretical analysis of the half-filled orbitals

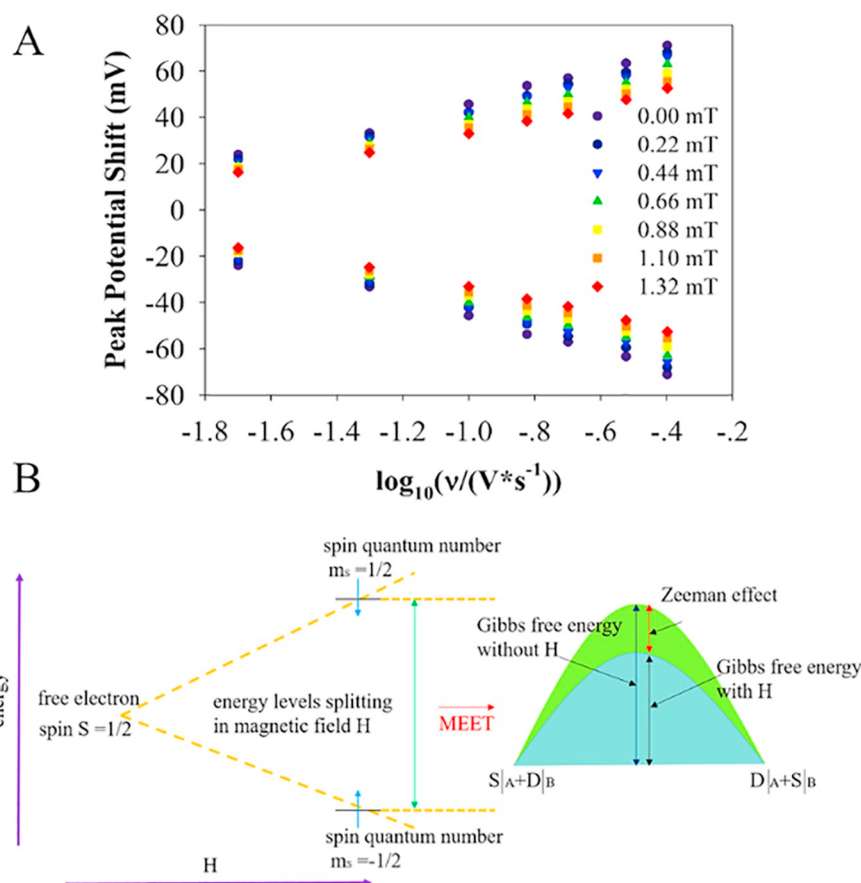


Fig. 4. (A) The dependence of the peak potential shift on the scan rate under different magnetic fields. (B) Diagram showing the energy levels and Zeeman effect.

Table 1

Electron-transfer rate constant data.

Magnetic field (mT)	Laviron method (s^{-1})	Extended Marcus method (0.05 eV) (s^{-1})	Extended Marcus method (0.10 eV) (s^{-1})	Extended Marcus method (0.20 eV) (s^{-1})
0.00	1.48 ± 0.17	0.94 ± 0.09	1.05 ± 0.13	1.17 ± 0.15
0.22	1.59 ± 0.14	1.06 ± 0.08	1.13 ± 0.10	1.27 ± 0.12
0.44	1.72 ± 0.09	1.12 ± 0.05	1.26 ± 0.07	1.36 ± 0.08
0.66	1.96 ± 0.12	1.20 ± 0.06	1.35 ± 0.09	1.43 ± 0.10
0.88	2.14 ± 0.18	1.32 ± 0.12	1.46 ± 0.16	1.59 ± 0.19
1.10	2.28 ± 0.16	1.46 ± 0.08	1.66 ± 0.11	1.74 ± 0.14
1.32	2.40 ± 0.07	1.73 ± 0.03	1.87 ± 0.04	2.04 ± 0.06

in electrocatalysis suggests that the charge-transfer rate shows spin dependence under a magnetic field [32]. Hence, one can conclude that the effect of magnetic field polarization on unpaired electron spin-orbital coupling and the energy degeneracy would facilitate electron transfer in the galvinoxyl-gold electrode system, providing more evidence of the magnetic susceptibility of galvinoxyl radicals.

4. Conclusions

This work demonstrates that the presence of a magnetic field can influence electron transfer in the galvinoxyl-gold electrode system. Cyclic voltammetry studies show a change in peak potential shift as the magnetic field increases, and the electron-transfer rate constants are obtained by the Laviron method and the extended Marcus model. These results both support the postulated magnetic susceptibility of the system with its ultrathin film structure, which may open an avenue to novel ferromagnetic organic layer applications.

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