Abnormal Magnetic Field Effects on Electrogenerated Chemiluminescence

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We report abnormal magnetic field effects on electrogenerated chemiluminescence (MFE ECL) based on triplet emission from the Ru(bpy)₃Cl₂⋯TPrA electrochemical system: the appearance of MFE ECL after magnetic field ceases. In early studies the normal MFE ECL have been observed from electrochemical systems during the application of magnetic field. Here, the abnormal MFE ECL suggest that the activated charge-transfer [Ru(bpy)₃]³⁺⋯TPrA⁻] complexes may become magnetized in magnetic field and experience a long magnetic relaxation after removing magnetic field. Our analysis indicates that the magnetic relaxation can gradually increase the density of charge-transfer complexes within reaction region due to decayed magnetic interactions, leading to a positive component in the abnormal MFE ECL. On the other hand, the magnetic relaxation facilitates an inverse conversion from triplets to singlets within charge-transfer complexes. The inverse triplet → singlet conversion reduces the density of triplet light-emitting states through charge-transfer complexes and gives rise to a negative component in the abnormal MFE ECL. Nevertheless, our experimental studies may reveal un-usual magnetic behaviors with long magnetic relaxation from the activated charge-transfer [Ru(bpy)₃]³⁺⋯TPrA⁻] complexes in solution at room temperature.

The magnetic field effects on electrogenerated chemiluminescence intensity, known as MFE ECL, have been intensively used to investigate the spin-dependent reaction routes in electrochemical reactions³⁻⁵. The most important step of generating electrogenerated chemiluminescence (ECL) can be formulated as the intermolecular electron transfer between strong reductant A – and oxidant D⁺ (A – + D⁺ → A⁺ + D) in electrochemical reactions³⁻⁵. In general, the MFE ECL can be generated through two different channels, the so-called density and conversion channels, as shown in Fig. 1a. In the density channel, a magnetic field can change the density of light-emitting states by exerting Lorentz and magnetizing forces on reactant radicals (A – and D⁺) and altering the total density of reactants in the reaction zone, generating density-based MFE ECL. In the conversion channel, the conversion between singlets and triplets in both intermediate charge-transfer [A–⋯D⁺] complexes and light emitting states may be modified by an applied magnetic field through spin mixing⁶⁻⁷, leading to conversion-based MFE ECL. It should be noted that the density-based MFE ECL usually occurs on intermediate activated charge-transfer [A–⋯D⁺] complexes, regarded as the precursor to the light-emitting states, because the Lorentz and magnetizing forces can be normally applied onto radical ions. Essentially, the change in the density of charge-transfer [A–⋯D⁺] complexes can lead to a modification on the concentration of light-emitting states (A⁺) within reaction zone for the development of density-based MFE ECL. On the other hand, the conversion-based MFE ECL can be, in principle, generated through both charge-transfer complexes and light-emitting states. In charge-transfer complexes a magnetic field can conveniently change the conversion between singlets and triplets by modifying the singlet-triplet intersystem crossing through spin mixing, eventually changing the singlet and triplet populations of light-emitting states. In light-emitting states, an external magnetic field is not able to disturb the singlet-triplet intersystem crossing due to the strong spin-exchange interaction and spin-orbital coupling within the Ru(bpy)₃Cl₂⋯TPrA⁻ in our system. But an applied magnetic field can change triplet-triplet annihilation⁸⁻¹⁰¹¹ and triplet-charge reaction in light-emitting states. This can cause a change on the population of light-emitting triplets for the development of conversion-based MFE ECL. Therefore, the conversion-based MFE ECL can involve in both charge-transfer complexes and light-emitting states including (i) the conversion between singlets and triplets in charge-transfer complexes, and (ii) triplet-triplet annihilation and triplet-charge reaction in light-emitting states. However, it has been shown that the conversion in charge-transfer complexes is a dominant component in the conversion-based MFE ECL. As a result, the overall MFE ECL can be mainly
**Figure 1** (a) MFE\textsubscript{ECL} are generated by density and conversion channels due to Lorentz and magnetizing force exerting on magnetized activated [A\textsuperscript{+} ... D\textsuperscript{+}] complexes within reaction zone. The ECL system used in our investigations contains tris(2,2'-bipyridine) ruthenium(II) (Ru(bpy)\textsubscript{3}\textsuperscript{2+}) and tertiary amines as coreactants. Here we choose tripropylamine (TPrA) because among many coreactants used in Ru(bpy)\textsubscript{3}\textsuperscript{2+} based ECL systems TPrA appears to produce the highest light levels\textsuperscript{15}. The universal ECL reaction routes of Ru(bpy)\textsubscript{3}\textsuperscript{3+} with tertiary amines can be expressed as Fig. 1b\textsuperscript{16,17}.

We can see from Fig. 1b that the electro-oxidation of TPrA generates a positively charged radical ion TPrA\textsuperscript{•+}. Then the \(\pi\)-carbon of TPrA\textsuperscript{•+} rapidly deprotonates to generate TPrA\textsuperscript{•}, which can be paired with the Ru(bpy)\textsubscript{3}\textsuperscript{3+} to form activated charge-transfer [Ru(bpy)\textsubscript{3}\textsuperscript{3+} ... TPrA\textsuperscript{•}] complexes for generating the light-emitting Ru(bpy)\textsubscript{3}\textsuperscript{2+}. It should be noted that the light emission is from the triplet Ru(bpy)\textsubscript{3}\textsuperscript{3+} which is controlled by the electron transfer process between activated radicals Ru(bpy)\textsubscript{3}\textsuperscript{3+} and TPrA \textsuperscript{•} within the charge-transfer [Ru(bpy)\textsubscript{3}\textsuperscript{3+} ... TPrA\textsuperscript{•}] complexes while the electrical current is governed only by the electron-oxidation and deprotonation of TPrA. Therefore, magnetic field effects on ECL intensity (MFE\textsubscript{ECL}) and electrical current (MC) can be used to distinguish the critical spin-dependent processes in this electrochemical system.

**Results and Discussion**

Fig. 2a shows the MFE\textsubscript{ECL} and MC generated from the electrochemical Ru(bpy)\textsubscript{3}\textsuperscript{2+} - TPrA system. The observed magnetic field effects can be divided into two regimes: during the application of magnetic field and after ceasing magnetic field. In normal regime, both MFE\textsubscript{ECL} and MC signals follow the profile of magnetic field, generating positive magnetic field effects. However, in abnormal regime the two signals show different behaviors: the MFE\textsubscript{ECL} signal increases to reach a second peak and then gradually decays to zero while the MC signal gradually decreases to zero, after the applied magnetic field ceases. Usually, the magnetic field effects only appear during the application of a magnetic field\textsuperscript{16,17,35,36}, which are named as normal MFE\textsubscript{ECL} and MC. Here, we can see from Fig. 2a that the MFE\textsubscript{ECL} show an abnormal phenomenon: light intensity increases and then decreases after ceasing magnetic field at a constant electrochemical condition. We name this phenomenon as abnormal MFE\textsubscript{ECL}. To our best knowledge, it is the first time to report abnormal MFE\textsubscript{ECL} after an applied magnetic field is removed. It is obvious that in abnormal regime the MFE\textsubscript{ECL} and MC show very distinct behaviors with significant and negligible values, respectively (Fig. 2a). This distinct difference indicates that the MFE\textsubscript{ECL} and MC can be attributed to charge-transfer [Ru(bpy)\textsubscript{3}\textsuperscript{3+} ... TPrA\textsuperscript{•}] complexes and TPrA\textsuperscript{•}, separately. The abnormal MFE\textsubscript{ECL} may imply that the intermediate activated charge-transfer [Ru(bpy)\textsubscript{3}\textsuperscript{3+} ... TPrA\textsuperscript{•}] complexes still experience magnetic interactions after applied magnetic field is removed, which changes the concentration of light-emitting states within reaction zone. Based on this analysis, we can suggest that the charge-transfer [Ru(bpy)\textsubscript{3}\textsuperscript{3+} ... TPrA\textsuperscript{•}] complexes may become magnetized during the application of magnetic field and then undergo a long magnetic relaxation after applied magnetic field ceases. Generally, the magnetic relaxation after ceasing magnetic field can affect both the density of charge-transfer complexes and the conversion between singlets and triplets within charge-transfer complexes, generating abnormal MFE\textsubscript{ECL} (Fig. 2d). First, upon ceasing magnetic field the magnetic relaxation can gradually decrease the magnetic interaction between the charge-transfer complexes, disturbing the density equilibrium within reaction zone previously established by the competition between magnetizing force and diffusion force during the application of magnetic field (Fig. 2c). Disturbing the density...
Figure 2 | (a) MFE\textsubscript{ECL} and MC are shown at a constant electrode-potential of 1.28 V rapidly changed from low 1.11 V. (b) Experimental setup for MFE\textsubscript{ECL}/MC measurements by placing an electrochemical cell in a magnetic field. (c) Activated charge-transfer (CT) \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes are subject to both diffusion and magnetizing forces in reaction zone. Removing an external magnetic field can break the previously established equilibrium on the CT density, consequently leading to an increase on the mass transport of reactants with the consequence of increasing electrochemical equilibrium. Therefore, density-based \textsuperscript{+}MFE\textsubscript{density} and conversion-based \textsuperscript{−}MFE\textsubscript{conversion} generate the non-monotonic curve of abnormal MFE\textsubscript{ECL}.

We should note that only normal MC is observed in our system. Because MC is generated by Lorentz force or spin polarization effects. Here, our measurements were performed at the zero angle condition between magnetic field and charge transport (Fig. 2b). Additionally, the observed MC does not show appreciable angle dependence when the angle between magnetic field and charge transport is changed. Thus Lorentz force can be neglected in our system. This leaves the spin polarization effects responsible for the observed MC. In principle, spin polarization can increase the formation of TPrA\textsuperscript{−} radicals by decreasing the C-H bond recovery through spin configuration effects\textsuperscript{13} in electrochemical reaction. This can cause an increase on the oxidation rate of TPrA on working electrode, leading to an increase on electrical current upon applying a magnetic field. Therefore, the spin polarization effects of TPrA\textsuperscript{−} radicals can generate a positive MC. Clearly, the MC results (Fig. 3) confirm that the TPrA\textsuperscript{−} radicals are spin polarized in a magnetic field. In particular, the spin polarization of TPrA\textsuperscript{−} radicals provides a pre-condition for the charge-transfer \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes to become magnetized with abnormal MFE\textsubscript{ECL} in the electrochemical system.

Now we discuss the possible mechanism to generate the magnetized charge-transfer \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes. It is noted that the distance between the oxidant Ru(bpy)\textsubscript{3}\textsuperscript{3+} and reductant TPrA\textsuperscript{−} during the electron transfer process is usually in the range of 4–6 Å\textsuperscript{4}. Thus, the \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes are often defined as activated charge-transfer complexes. In this situation, the molecular orbitals may overlap to generate the intermolecular contacts between the nitrogen \(\pi\) orbitals of TPrA\textsuperscript{−} and the bpy \(\pi\) orbitals of Ru(bpy)\textsubscript{3}\textsuperscript{3+} in charge-transfer \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes. It has been found that the overlap of molecular orbitals in several stacking modes of allyl and nitroxide radical systems play an essential role in generating ferromagnetic interaction in extended molecular systems\textsuperscript{18–20}. The literature work has also found that the intermolecular contacts between the NO groups and the phenyl ring may also assist the ferromagnetic interaction in spin radicals. Therefore, we can expect a possible ferromagnetic interaction in our charge-transfer \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes in an applied magnetic field. In addition, it has been shown that the ferromagnetic interaction can possibly occur between charge-transfer complexes due to the overlap of spatially extended wavefunctions\textsuperscript{21–23}. As a result, the charge-transfer \textit{[Ru(bpy)\textsubscript{3}]\textsuperscript{3+}... TPrA\textsuperscript{−}} complexes can be comparable to generating a negative component in abnormal MFE\textsubscript{ECL} (\textsuperscript{−}MFE\textsubscript{T→S}) through conversion channel. Therefore, the density-based \textsuperscript{+}MFE\textsubscript{density} and conversion-based \textsuperscript{−}MFE\textsubscript{conversion} generate the non-monotonic curve of abnormal MFE\textsubscript{ECL}.

Figure 3 | MC from two different electrochemical systems: (Ru(bpy)\textsubscript{3})\textsubscript{Cl\textsubscript{2}} + TPrA and TPrA\textsuperscript{−} with the same applied electrode potential of 1.28 V. The two systems both use sodium dihydrogen phosphate as supporting electrolyte. The (Ru(bpy)\textsubscript{3})\textsubscript{Cl\textsubscript{2}} + TPrA system contains 1 mM Ru(bpy)\textsubscript{3}Cl\textsubscript{2} and 0.08 M TPrA as reactants. The TPrA\textsuperscript{−} system contains only 0.08 M TPrA as reactant.
the nitronyl nitroxide radicals which exhibit intermolecular ferromagnetic interaction due to the overlap of partially occupied molecular orbitals. It should be noted that the exchange coupling between the nitrogen π orbitals of TPrA and the bpy π orbitals of Ru(bpy)₃⁺ can be treated as a hybridization between Ru(bpy)₃⁺ and TPrA⁺. This hybridization is similar to the exchange coupling between π-conjugated orbitals on the quinoline rings and nitrogen π orbitals which generates ferromagnetic interaction between the spin moments. Therefore, the activated charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes may be magnetized due to (i) spin interactions of Ru(bpy)₃⁺ and TPrA⁺ radical ions and (ii) magnetic coupling between the charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes.

We should note that it is rare to observe magnetic interaction in charge-transfer complexes at room temperature. However, for some specific situation, magnetic coupling between two radicals which is connected to the same metal center can be obtained, forming molecular based ferromagnets at room temperature. In another case, a spontaneous magnetization can be induced from the exchange interactions between the localized spins on metal ion and the spins on organic radicals. In our ECL system, the possible magnetic coupling between [Ru(bpy)₃⁺ … TPrA⁺] complexes can be induced by (i) the spin interaction between Ru(bpy)₃⁺ and TPrA⁺ radicals due to the overlap between molecular orbitals of Ru(bpy)₃⁺ and TPrA⁺ within the charge-transfer complexes, (ii) the electron transfer from the nitrogen p orbitals of TPrA⁺ to the bpy π orbitals of Ru(bpy)₃⁺ and (iii) the orbital overlap between the charge-transfer complexes.

Next we discuss the critical parameters that can be accountable for magnetized charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes. We can see in Fig. 4a and 4b that the abnormal MFEECL are largely reduced when the electrode potential is slowly increased between selected potentials of 1.15 V and 1.43 V. In our system, the magnetic coupling require a high density of activated triplet charge-transfer complexes (with spin S = 1). Obviously, the largely reduced abnormal MFEECL upon slowly increasing electrical potential indicate the low density of charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes. This argument is made based on the following consideration. In general, a low electrode potential can lead to a low oxidation rate of reactants at the working electrode. In this case, the quantity of intermediate active radicals of Ru(bpy)₃⁺ and TPrA⁺ generated on the working electrode surface is low, diminishing the magnetic coupling. When the electrode potential is slowly increased to a high value, the reactants (mainly TPrA) are continuously consumed during the electrochemical process, as indicated by the little change in the oxidation current when applied electrode potential increases at slow-scan rate of 10 mV/s (Fig. 4c). In this case, at high electrode potential the quantity of oxidation products (mainly TPrA⁺) is still not high, leading to a low density of charge-transfer complexes and a negligible magnetic coupling between the activated charge-transfer complexes. In our experiments, the abnormal MFEECL can only be clearly observed when electrode potential rapidly changes from low to high value. In this case, there are a large amount of active radicals Ru(bpy)₃⁺ and TPrA⁺ generated nearby the working electrode at a short period of time, as indicated by the rapid enhancement of oxidation current as applied electrode potential increases at fast-scan rate of 100 mV/s (Fig. 4c). This condition can lead to a high density of activated charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes with magnetic coupling within the reaction zone to generate the abnormal MFEECL. Therefore, we can confirm that the high densities of both Ru(bpy)₃⁺ and TPrA⁺ in the reaction zone form a necessary condition to generate a strong magnetic coupling between the charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes. Essentially, strong magnetic coupling between the charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes generates magnetized charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes, leading to abnormal MFEECL. Furthermore, in order to observe the significant abnormal MFEECL, 1 mM Ru(bpy)₃Cl₂ is enough but the concentration of TPrA should be at least 0.08 M or higher.

Here we consider additional experimental evidence to support the possible magnetized charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes. Fig. 5a and 5b shows both normal and abnormal MFEECL at fast sweeping (32 mT/s) and slow sweeping (3.2 mT/s) rates. For the fast sweeping rate, the normal MFEECL peak (37%) coincides with the maximal value of applied magnetic field. However, the abnormal MFEECL Peak is decreased to 17%. For a slow sweeping rate, the peak (43%) of normal MFEECL appears before the maximum of applied magnetic field. The abnormal MFEECL peak remains at a high value (40%). The sweeping rate effects on both normal and abnormal MFEECL essentially reflect the possible magnetization response time during the application of magnetic field and the magnetic relaxation after the magnetic field is removed. During the application of magnetic field, the induced magnetization can decrease the density of charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes through repulsive magnetic interactions but increases the conversion from singlets to triplets within charge-transfer [Ru(bpy)₃⁺ … TPrA⁺] complexes, as indicated in Fig. 5c. In addition, the density and conversion-based MFEECL have negative and positive signs in normal regime, respectively. From the observed positive normal MFEECL, we can suggest that the singlet → triplet conversion is a major process at fast sweeping.
activated with the negative sign after the fast singlet with a slow sweeping rate the density component may be slowly reached.

towards the triplet formation of light-emitting states in the normal regime. This can give rise to a higher value for abnormal MFE ECL after removing magnetic field. The distinct behavior between MFE ECL and MC in abnormal regime confirm that the charge-transfer [Ru(bpy)3]2+...TPrA] complexes are magnetized species responsible for the abnormal MFE ECL in the electrochemical system. The magnetic relaxation after ceasing magnetic field generates two opposite effects: increasing the density of charge-transfer complexes due to decayed repulsive magnetic interactions and inducing an inverse triplet → singlet conversion due to gradually relaxed spin alignments in charge-transfer [Ru(bpy)3]2+...TPrA] complexes. The former and latter generate the density-based MFE density with positive sign and the conversion-based MFE conversion with negative sign in abnormal regime, respectively, after removing magnetic field. Clearly, our experimental studies on abnormal MFE may reveal magnetic coupling between intermediate activated charge-transfer [Ru(bpy)3]n+...TPrA] complexes with long magnetic relaxation in solution. The magnetic behavior can be attributed to the overlap of partially occupied orbitals initiated by electron transfer within the charge-transfer [Ru(bpy)3]n+...TPrA] complexes and the wavefunction overlaps between the charge-transfer [Ru(bpy)3]n+...TPrA] complexes at high density within reaction zone.

Methods

Based on the Ru(bpy)3Cl2-TPrA electrochemical system, we observe not only normal MFE ECL during the application of magnetic field but also abnormal MFE ECL after applied magnetic field ceases. The abnormal MFE ECL suggests that the charge-transfer [Ru(bpy)3]2+...TPrA] complexes may be magnetized in magnetic field and then experience a long magnetic relaxation after magnetic field is removed. On the other hand, we observe a negligible abnormal MC from this system after removing magnetic field. The distinct behavior between MFE ECL and MC in abnormal regime confirm that the charge-transfer [Ru(bpy)3]2+...TPrA] complexes are magnetized species responsible for the abnormal MFE ECL in the electrochemical system. The magnetic relaxation after ceasing magnetic field generates two opposite effects: increasing the density of charge-transfer complexes due to decayed repulsive magnetic interactions and inducing an inverse triplet → singlet conversion due to gradually relaxed spin alignments in charge-transfer [Ru(bpy)3]2+...TPrA] complexes.

Figure 5 | Normal and abnormal MFE ECL from the electrochemical (Ru(bpy)3)2Cl2 + TPrA) system under different field-sweeping rates at the electrode potential of 1.28 V. (a) Fast field-sweeping rate = 32 mT/s; (b) Slow field-sweeping rate = 3.2 mT/s. (c) Schematic diagram to show the generation of normal MFE ECL through density and conversion channels. [CT]B and [CT]0 are the densities of charge-transfer complex [Ru(bpy)3]2+...TPrA] before and during the application of a magnetic field.

MFEnormal = \frac{[CT]B - [CT]0}{[CT]0} + \frac{1}{\gamma} \frac{[CT]}{\gamma} = -\frac{MFE_{density}^N}{\gamma} + \frac{MFE_{conversion}^N}{\gamma}

The magnetic behavior can be attributed to the overlap of partially occupied orbitals initiated by electron transfer within the charge-transfer [Ru(bpy)3]n+...TPrA] complexes and the wavefunction overlaps between the charge-transfer [Ru(bpy)3]n+...TPrA] complexes at high density within reaction zone.

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Author contributions
H.P. did the experimental measurements. B.H. guided the research. B.H. and H.P. wrote the main manuscript text. Y.S., H.W. and I.H. revised the manuscript. All authors contributed to data analysis and discussions.

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