Tunable magnetic circular dichroism via electrochemically controlled charge-transfer transition in Ru(bpy)₃²⁺ aqueous solution

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ABSTRACT

Seeking potential aqueous solution with tunable magnetic properties by applied electrode potentials is an emerging research topic for the integration of aqueous solution into devices. In this work, $Ru(bpy)_3^{2+}$, which is widely used for high efficiency electroluminescent and photovoltaic devices, has been demonstrated as a potential liquid electrolyte with tunable magnetic properties by applied electrode potentials evidenced by energy resolved magnetic circular dichroism (MCD) spectroscopy. The MCD signal at 450 nm transforms from paramagnetic to nonmagnetic behavior when the applied electrode potentials are >1.3 V. The transition of the MCD signal from paramagnetic to nonmagnetic behavior is ascribed to the disappearance of metal to ligand charge transfer transition during the electrochemical oxidation process. This work might provide a valuable insight into exploration of functional liquid electrolyte with tunable opto-magnetic properties.

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To manipulate the magnetic-related phenomena of a material with the help of electric fields is an important and rapidly developing research area in modern magnetism, in both fundamental science and emerging applications.^{1–3} Voltage (V) control of magneto-resistance, magnetic anisotropy, and magnetization in a solid state device with a ferromagnetic layer exchange-coupled to a non-magnetic solid dielectric layer has been demonstrated in the last few decades.^{2,4,5} However, in solid state devices, the dielectric breakdown due to pinholes or defects is very difficult to avoid.

On the other hand, in liquid systems, the charge accumulation induced by an applied electric field at the material-liquid interface can also modulate the magnetic properties similar to that of the materialsolid interface.^{6–8} In addition, while a ferromagnetic material is used as a magnetic electrode in an electrochemical system containing freely moving ions, cation intercalation due to applied electrode potentials could also affect the magnetic properties of the ferromagnetic material.⁹ The operation mechanism is similar to lithium-ion batteries or other energy storage systems.^{9,10} The small ions, such as Na⁺ or Li⁺, are responsible for cation intercalation. Because these material-liquid electrolyte systems do not undergo as much dielectric breakdown, it attracts a lot of interest to seek suitable liquid electrolytes, which can be integrated into solid devices.¹¹⁻¹⁴

In general, variations of magnetism in liquid electrolyte-gated configurations may be related to charge accumulation or cation intercalation, as mentioned above. However, the disadvantage of charge accumulation is that it is only sensitive on the accessible surface area of ferromagnetic materials. Furthermore, cation intercalation is a relatively slow process and the insertion and removal of ions from the ferromagnetic materials can result in the mechanical failure over time after a few cycle operations due to the degradation. Therefore, a fundamental question raises: could we find a functional aqueous solution whose magnetism can be directly controlled during the electrochemical process without integration of ferromagnetic materials?

Here, Ruthenium(II)-tris-2,2'-bipyridine $[Ru(bpy)_3^{2+}]$ could serve as a potential aqueous solution with tunable magnetic properties by applied electrode potentials, without integration of any solid magnetic materials. $Ru(bpy)_3^{2+}$ exemplifies a model system of intramolecular electron transfer reactions.¹⁵⁻¹⁷ $Ru(bpy)_3^{2+}$ has been studied



intensively because of possible applications of its metal to ligand charge transfer (MLCT) excited states in solar energy conversion and storage processes.¹⁸⁻²¹ For example, in dye-sensitized solar cells, the efficient photoexcited electron transfer from the MLCT manifold to the conduction band of a semiconductor electrode is allowed by its low-lying excited states.²¹ Although Ru(bpy)₃²⁺ is one of the deepest studied transition-metal complexes, whose electrochemistry and photochemistry have obtained a complete understanding, the studies of its magnetic properties during electrochemical and photochemical processes are rare. Furthermore, such kinds of magnetic properties of aqueous solution are very difficult to measure by the typical magnetic method, such as a superconducting quantum interference device (SQUID), or magneto-transport measurements. Here, magneto-optical spectroscopy, namely, energy resolved magnetic circular dichroism (MCD), which is the absorption difference between right circular polarized light and left circular polarized light, could be used as a suitable technique to study this issue.

In this work, transition from the paramagnetic to non-magnetic state of $\text{Ru}(\text{by})_3^{2+}$ -based aqueous solution can be reversed by controlling the applied electrode potentials in the electrochemical oxidation process at room temperature. The mechanism can be associated with the disappearance of MLCT transition in electrochemical generated $\text{Ru}(\text{by})_3^{3+}$ radical ions evidenced by using the operando energy resolved MCD technique. The significant changes in magnetism of $\text{Ru}(\text{by})_3^{2+}$ -based aqueous solution provide strong design-on-demand properties for electrical manipulation of magneto-optical characteristics in liquid electrolyte devices without integration of any solid magnetic materials.

Figure 1(a) shows the planar molecular structure of $Ru(bpy)_3Cl_2$, stereostructure of Ru(bpy)₃²⁺, and its corresponding orbital diagram. With respect to both theoretical predictions and experimental analyses, the orbital diagram of $Ru(bpy)_3^{2+}$ has been studied in detail.² Figures 1(b)-1(e) reveal the operando absorption spectra of the Ru(bpy)₃²⁺ complex dissolved in aqueous solution during electrochemical oxidation at 0V, 1.1V, and 1.2V (vs Ag/AgCl) applied electrode potentials. There are three main absorption bands, which peak at 243 nm, 285 nm, and 450 nm, respectively. The absorption peak at 285 nm is easily assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions by comparison with the absorption spectrum of the protonated bipyridine ligand.²² The other two peaks at 243 nm and 450 nm could be assigned to ligand-to-metal charge-transfer (LMCT) and metal-toligand charge-transfer (MLCT) transitions, respectively.²²⁻²⁵ It is noted that the MLCT transition involves a metal-centered valence electron transferring from its singlet ground state to the lowest-energy absorption band and localization of the electron on one of the bipyridine ligands.¹⁵ The charge transfer process leads to both electronic and geometric changes in the $Ru(bpy)_3^{2+}$ complex, which may be related to changes in magnetic properties. Here, we will show how we can control the magnetic properties of Ru(bpy)₃²⁺-based aqueous solution through MLCT transitions by using the operando optical absorption and energy resolved MCD spectroscopy.

When the electrode potentials are applied to the electrodes of the spectroelectrochemical cell, the oxidation process $[Ru(bpy)_3^{2+} - e \rightarrow Ru(bpy)_3^{3+}]$ could occur in $Ru(bpy)_3^{2+}$ -based aqueous solution.²⁶ The metal ion Ru in the $Ru(bpy)_3^{2+}$ complex loses an electron in the d orbital to the working electrode and generates a $Ru^{III}(bpy)_3^{3+}$ radical ion.^{23,27} When the applied electrode potential is low, for instance,



FIG. 1. (a) The planar molecular structure of the Ru(bpy)₃Cl₂, stereostructure of Ru(bpy)₃²⁺ and its corresponding orbital diagram. (b)–(e) are optical absorption spectra of Ru(bpy)₃²⁺-based aqueous solution collected during electrolysis at different applied electrode potentials. The aqueous solution contained 0.4 mM Ru(bpy)₃Cl₂ and 0.1 M NaH₂PO₄. The absorption peak at 285 nm (\bullet) could be assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions. The absorption peaks red-shifted (\bigcirc) and the absorption band broadening indicates the electronic and geometric changes in the Ru^{III}(bpy)₃³⁺ radical ion. The other two remaining intense absorption peaks, at 243 nm (\bullet) and 450 nm (\mathbf{V}), could be assigned to metal-to-ligand (or vice versa) charge-transfer (MLCT or LMCT) transitions.

1.1 V and 1.2 V, the energy level of the working electrode is higher than the d orbital in the Ru(bpy)₃²⁺ complex.²⁸ The resulting electrochemical oxidation rate, which is related to the transferring electrons from the d orbital to the working electrode, is low (Fig. 2). Thus, the main component of the solution is still in Ru(bpy)₃²⁺ ground states. Compared with the absorption spectrum of 0 V, no significant change in the optical absorption spectra at 1.1 V and 1.2 V confirms this result [as shown in Fig. 1(b)]. However, as the applied electrode potential further increases [approaching or exceeding the oxidation potential of +1.3 V (vs Ag/AgCl)^{29,30}], the energy level of the working electrode becomes lower than the d orbital in the Ru(bpy)₃²⁺ complex. Therefore, the electrons transferred from the d orbital to the working electrode increase significantly and high oxidation current is generated (Fig. 2). As a result, the electrochemical oxidation rate of Ru(bpy)₃³⁺ radical ion increases rapidly. Consequently, the concentration of electrochemical generated Ru(bpy)₃³⁺ radical



FIG. 2. The cyclic voltammogram of $Ru(bpy)_3^{2+}$ -based aqueous solution (containing 0.4 mM $Ru(bpy)_3Cl_2$ and 0.1 M NaH_2PO_4) at a platinum gauze working electrode (scan rate 100 mV/s).

ions in the electrochemical cell rises accordingly at high applied electrode potentials (for instance, 1.3 V, 1.4 V, and 1.5 V), which leads to a significant change on the absorption spectra compared with that of low applied electrode potentials [Fig. 1(c)-1(e)]. The phenomenon comes from the oxidation potential of +1.3 V (vs Ag/AgCl)^{29,30} and is consistent with our cyclic voltammogram of Ru(bpy)₃²⁺-based aqueous solution in Fig. 2.

The peak intensity of absorption spectra at 450 nm decreases rapidly in solution, which contains mainly Ru(bpy)₃³⁺ radical ions at 1.5 V (as shown in Fig. 3). This suggests that the absorption band at 450 nm is MLCT ($d \rightarrow \pi^*$) transition. Due to the metal ion Ru already losing an electron in the d orbital at the electrochemical oxidation process to generate Ru^{III}(bpy)₃³⁺, which is a d⁵ complex,³¹ stabilized and not easily being photoexcited, the probability of MLCT transition significantly decreases in Ru^{III}(bpy)₃³⁺ radical ions. This leads to a rapid decrease in absorption peak intensity at 450 nm. Meanwhile, the absorption peak intensity at 243 nm gradually increases as the applied electrode potential further increases (Fig. 3). The absorption peak intensity at 243 nm increases by about 20% at 1.5 V, which contains mainly Ru^{III}(bpy)₃³⁺ radical ions in solution. This result suggests that the absorption band at 243 nm could be attributed to LMCT ($\pi \rightarrow d^*$) transition. The loss of an electron in the d orbital of Ru will result in more unoccupied states in the Ru^{III}(bpy)₃³⁺ radical ion and thus enhance the LMCT ($\pi \rightarrow d^*$) transition-related absorption.



FIG. 3. The absorption intensity vs electrode potential at 450 nm and 243 nm of Ru(bpy)_3^{2+} -based aqueous solution during electrolysis is shown.

Furthermore, the absorption peak at 285 nm ($\pi \rightarrow \pi^*$ transition) is redshifted to 300 nm and the peak intensity drops for Ru^{III}(bpy)₃³⁺ radical ions compared with Ru^{II}(bpy)₃²⁺ ground states [as shown in Fig. 1(e)]. This is ascribed to the change in ligand geometry, mainly due to the variation in the angle between the two bipyridine rings owing to the increased charge of the central Ru ion.^{20,32} It leads to weaker interaction between the pyridine rings, which primarily controls the energy and rate of $\pi \rightarrow \pi^*$ transitions.³² Thus, the absorption peaks are redshifted, and the peak intensity decreases for Ru^{III}(bpy)₃³⁺ radical ions due to the changes of geometric and electronic structures of the bpy ligand in Ru^{III}(bpy)₃³⁺ radical ions. Both the geometric and electronic changes in the Ru^{III}(bpy)₃³⁺ radical ion compared with those of Ru(bpy)₃²⁺ ground states may lead to changes in magnetic properties.

To further confirm that the magnetic properties of Ru(byy)₃²⁺based aqueous solution could be manipulated by electrochemical oxidation, we measured the energy resolved MCD intensity of Ru(byy)₃²⁺-based aqueous solution during electrochemical oxidation at different applied electrode potentials. Figure 4 depicts the MCD intensity monitored at 450 nm over a B = ±0.8 T field range at different applied electrode potentials. When the applied electrode potentials were low (≤ 1.2 V), the magnetic field-dependent MCD (MCD-H) curves behave as paramagnetic curves [Figs. 4(a)–4(c)]. Because the MCD signals at 450 nm can be related to MLCT transition (d $\rightarrow \pi^*$) as discussed above, the origin of paramagnetic MCD curves should come from the photoexcited electron in π^* states. The slopes of the MCD-H curves are similar. The results are consistent with the absorption characterization that the absorption intensities are similar when the applied electrode potentials were low [≤ 1.2 V, Fig. 1(b)].

Interestingly, as the applied electrode potentials further increase until it exceeds 1.2 V (1.3 V, 1.4 V, and 1.5 V), the slopes of the MCD-H curves decrease significantly with increasing applied electrode potentials (Fig. 5). For instance, the values of the MCD slope at 1.3 V, 1.4 V, and 1.5 V are 1.61, 0.11, and 0.17, far less than the value at 1.1 V and 1.2 V (4.95 and 4.76). The significant decrease in the slope confirmed the transformation process from paramagnetic to nonmagnetic behavior as applied electrode potentials increase. These results further demonstrated that the central metal core Ru of $Ru(bpy)_3^{2+}$ complexes has lost an electron in the electrochemical oxidation process and generated a large amount of Ru^{III}(bpy)₃³⁺ radical ions, which is a stabilized d⁵ complex. The probability of the photoexcited electron transfer process in the stabilized d⁵ complex is low. Thus, the transformation from paramagnetic MCD-H to nonmagnetic MCD-H behavior, which was observed during the electrochemical oxidation process $[Ru(bpy)_3^{2+}-e \rightarrow Ru^{III}(bpy)_3^{3+}]$, further indicates that the photoexcited electron could be the origin of paramagnetic properties. Therefore, the lack of photoexcited electrons in the solution while the applied electrode potentials exceed 1.4 V reveals a non-magnetic behavior and does not show the paramagnetic MCD effect.

Since the MCD effect indicates the change in optical polarization, it implies that the optical polarization under an applied magnetic field can be tuned and suppressed by electric bias. Our results could offer strong design-on-demand characteristics for electrically manipulated magneto-optical devices based on $\text{Ru}(\text{bpy})_3^{2+}$ aqueous solution, as shown in Fig. 5. It is noted that such variations in magnetic properties of $\text{Ru}(\text{bpy})_3^{2+}$ -based aqueous solution could be related to charge transfer transition during the electrochemical oxidation process. In



FIG. 4. The MCD intensities vs H recorded at 450 nm of Ru(bpy)₃²⁺-based aqueous solution during electrolysis obtained at (a) 0 V, (b) 1.1 V, (c) 1.2 V, (d) 1.3 V, (e) 1.4 V, and (f) 1.5 V.

comparison with material-liquid electrolyte systems whose magnetism could be manipulated by cation intercalation, there are some advantages in our liquid electrolyte-only system whose magnetism is controlled by the electrochemical oxidation process. The electrochemical process in the liquid electrolyte does not cause material degradation and mechanical failure over time. On the other hand, the magnetic signal change ratio is generally limited by the accessible surface area in material-liquid electrolyte systems via cation intercalation. Here, a significant magnetic signal change ratio (\sim 100%) due to transformation from paramagnetic to non- magnetic behavior could be observed in our electrolyte-only system. In addition, the reaction time of charge transfer in the electrochemical process is much faster than that of cation intercalation in material-liquid electrolyte systems. Such a



FIG. 5. The MCD slope vs applied electrode potential of Ru(bpy)₃²⁺-based aqueous solution during electrolysis is shown. The transformation from paramagnetic to non-magnetic behavior can be observed as the applied electrode potentials exceed 1.4 V. It indicates that the Ru(bpy)₃²⁺ aqueous solution could be used for electrically controlled polarization devices under an applied magnetic field. The suppression of MLCT transition (d $\rightarrow \pi^*$) at 450 nm should be responsible for the transformation.

functional liquid electrolyte, in conjunction with electrode potentialtunable MCD signals, can be devised to design magneto-optical and magneto-optoelectronic devices.

In summary, the $Ru(bpy)_3^{2+}$ -based aqueous solution has been demonstrated as a potential aqueous solution with tunable magnetic properties by applied electrode potentials evidenced by energy resolved MCD spectra. Furthermore, the accompanying MCD signal at 450 nm transforms from paramagnetic to non-magnetic MCD-H behaviors as applied electrode potentials further increase. The transformation behaviors could be reversed by tuning applied electrode potentials during the electrochemical oxidation process. These findings pave the way toward further exploration of the functional liquid electrolyte with tunable opto-magnetic properties and lead to the development of magnetic field-manipulation of photovoltaic and electroluminescent devices.

See the supplementary material for the experimental description and setup (Fig. S1) for optical absorption and energy resolved MCD spectra measurements.

AUTHORS' CONTRIBUTIONS

H.-P.P. performed the experimental measurements and analysis. Y.-H.H. helped with the magnetic circular dichroism (MCD) measurements. H.-S.H. designed operando-MCD experiments. H.-P.P., H.-S.H., and M.-T.L. wrote the manuscript. M.-T.L. conceived the idea and supervised the whole project.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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