Utilization of Electrochromically Luminescent Transition-Metal Complexes for Erasable Information Recording and Temperature-Related Information Protection

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Stimulus-responsive materials have been drawing great research interest in the design and development of novel memory devices,[1–4] sensors,[5,6] biomedicine,[7,8] security materials,[9,10] and information displays.[11–14] Among these materials, those exhibiting remarkable response to an electrical stimulus have received particular attention because they are readily incorporated into electronic devices for a variety of applications.[1–3,8,14–17] Pyridinium derivatives such as viologens are a family of the most widely used electrical-responsive dyes, in which electrochromism is modulated by redox processes.[14,18–23] Under certain voltages, they undergo reversible conversions between the cationic and radical forms, giving an absorption change in the visible region, realizing information recording. To ensure that a remarkable color change, i.e., the recorded information, can be recognized by naked eyes, a relatively high concentration in the millimolar scale of pyridiniums is usually required. As a possible output signal, luminescence is considered as one of the most attractive reading signals since light can be detected with exquisitely high sensitivity. The working concentrations of molecular dyes that reflect external stimuli into luminescence signals are usually as low as micromolars or nanomolars depending on their luminescence quantum efficiencies.

Phosphorescent transition-metal complexes have been extensively studied and employed for the photonic and electronic applications owing to their advantageous photophysical properties, such as high emission quantum yields, long emission lifetimes, large Stokes shifts, high photostability, tunable emission colors, and extremely high sensitivity toward ligand structures and surrounding microenvironment.[24–26] Recently, we have designed a series of phosphorescent iridium(III) complexes whose emission colors are sensitive to electric field-induced migration of the anionic counterions.[10] These complexes have been used to develop an information recording and storage device. However, the recorded information cannot be easily erased due to the difficulty in the reversible control of ion migration in devices.

Studies of transition-metal complexes with pendant pyridine or pyridinium moieties showed that the luminescence of the transition-metal complexes is efficiently quenched by the electron deficient pyridiniums via photoinduced oxidative electron-transfer.[27–31] In this work, we hypothesize that reduction of the pyridiniums by electric stimulus or reducing agents yielding radicals will break the electronic communication with the excited transition-metal complexes cores and hence turn on the luminescence. Since pyridinium derivatives undergo completely reversible redox-controlled conversion between cationic and radical forms,[17–22] the luminescence can reversibly be turned on and off upon electrochemical reduction and oxidation, respectively, which indicates the potential application of these transition-metal complexes in erasable electronic information recording devices.

Three iridium(III) and one ruthenium(II) complexes containing pendant pyrazinium or pyridinium including newly synthesized complexes **1** and **2** and previously reported complexes **3** and **4**[30] (**Scheme 1**) have been synthesized to study their luminescence response toward the electric stimulus. Bipyrazine and quaterpyridine have been used as the diimine ligand and synthesized according to reported procedures.[32,33] After coordination to transition-metal centers, diquaternization with methyl iodide yielded pyraziniums and pyridiniums, respectively. The analogues **1a**–**4a** without methylation have also been prepared for comparison study. All the complexes have been characterized via proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy, infrared (IR) spectroscopy, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), and UV–visible absorption spectroscopy (see the Supporting Information, Figure S1). The ^{1}H NMR spectra of complexes **1**–**4** revealed a singlet signal at 4.20–4.38 Hz, respectively, corresponding to the six protons of the two methyl groups. The absorption bands of all the complexes have been assigned to spin-allowed singlet intraligand (^{1}IL), metal-to-ligand charge-transfer (^{1}MLCT), and ligand-to-ligand change-transfer transitions.

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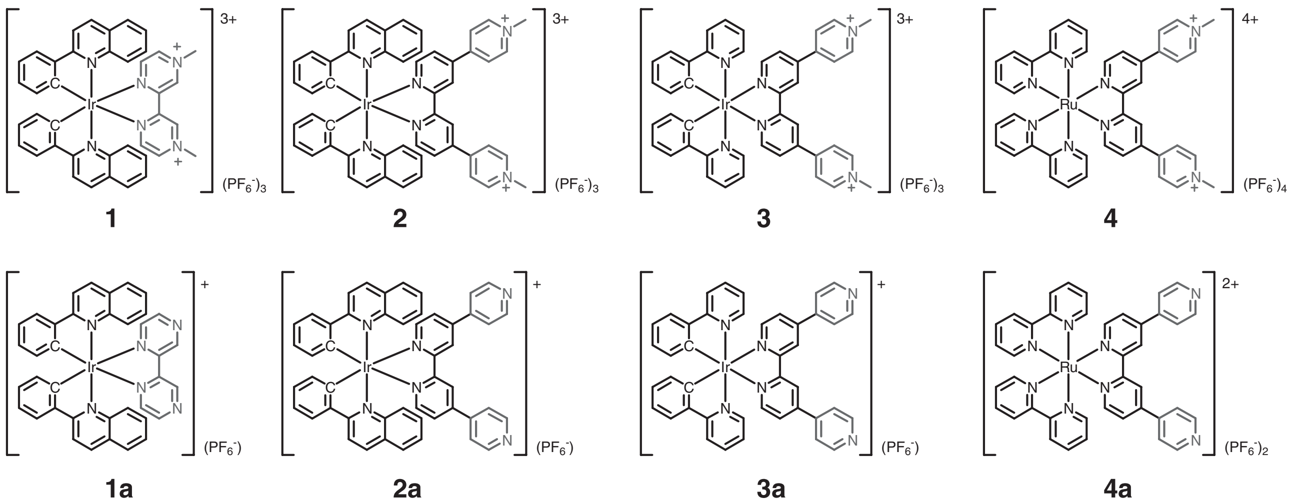

Scheme 1. Chemical structures of the complexes.

The electrochemical properties of all the complexes were studied via cyclic voltammetry. The electrochemical data are summarized in Table S1 (Supporting Information). The metal-based oxidation couples occurred at about +1.31 to +1.34 V and +1.25 V versus saturated calomel electrode (SCE) for the iridium(III) and ruthenium(II) complexes, respectively. The pyrazinium complex **1** displayed the first reduction at −0.89 V and the pyridinium complexes **2**–**4** displayed two unresolved reduction couples at about −0.67 to −0.79 V. These couples were completely reversible and no variation in the potential was observed after 50 cycles of redox scanning (Figure S2, Supporting Information). Since these couples were not observed for complexes **1a**–**4a**, they have been assigned to the reduction of the pyrazinium and pyridinium units. The reduction waves appearing at more negative potentials have been assigned to the reduction of the ligands. The occurrence of the pyridinium-based reduction rendered the reduction of the ligands of complexes **1**–**4** more difficult compared to that of complexes **1a**–**4a** (Table S1, Supporting Information). Upon photoexcitation, complexes **1a**–**4a** exhibited orange to near infrared luminescence, which typically emanated from the triplet ^{3}MLCT excited state mixed with some ^{3}IL character. The luminescence spectra are shown in Figure S3 (Supporting Information) and the luminescence data are summarized in Table S1 (Supporting Information). As expected, the methylated complexes **1**–**4** were nonemissive or weakly emissive owing to the efficient quenching by the electron deficient pyridiniums via photoinduced oxidative electron-transfer. Since the luminescence intensity of the methylated complexes was linearly proportional to the complex concentration in the range of 10×10^{-6} to 1×10^{-3} M with the luminescence lifetime independent of the concentration, it is likely that the luminescence quenching was an intramolecular process.

The luminescence response of all the complexes toward an electrical stimulus has been investigated. As illustrated in **Figure 1**a, into a solution of complex **2** (10×10^{-6} M) and nBu_4NPF_6 (0.1 M) in acetonitrile were immersed two tin electrodes with a distance of 2 cm between each other. Upon applying a voltage of 3 V, the photoluminescence of the solution at the cathode half side was gradually turned on and the solution at the anode remained nonemissive, revealing a clear boundary in the middle of the cuvette (Figure 1b). This is because reduction of the methylpyridinium units occurred at the cathode, which prevented the oxidative quenching of the excited complex. Different from many other viologen-based electrochromic materials,[14,16,17] the absorption spectra of the complex in the visible region did not show noticeable change and the generation of radicals cannot be captured in the electron spin resonance experiments because of a much lower concentration of the complex. Once reversing the direction of the voltage, the cathode and anode were exchanged and the luminescent side was turned off and the nonemissive side was turned on because of the oxidation and the reduction that occurred at the two sides, respectively (Figure 1b). Restoring the direction of the voltage recovered the luminescence at the cathode and quenched the luminescence at the anode (Figure 1b). The electrochromic luminescence has also been observed when using complexes **1**, **3**, and **4**, but the methylation-free complexes **1a**–**4a** did not show similar phenomenon, which indicated that the interesting electrochromic luminescence was brought about by the reversible redox reaction of pyrazinium and pyridinium moieties.

To investigate the luminescence response of the methylated complexes to electrical stimuli in detail, a salt-bridge composed of agarose hydrogel containing $^nBu_4NPF_6$ has been used to separate the solutions linked to the cathode and anode (Figure 1c), and hence the luminescence spectra of the complex solutions at the cathode and anode can be recorded and analyzed quantitatively. As shown in Figure 1d, the luminescence intensity of complex **2** at the cathode was enhanced by about 26 fold upon applying a voltage of 10 V for 30 min, while at the anode the solution remained nonemissive and the intensity variation was less than ±10% (Figure S4, Supporting Information). Similar electrochromic luminescence has also been observed for complexes **1**, **3**, and **4** (Figure S5–S7, Supporting Information). Interestingly, the electrochromic luminescence turn-on of the cathode solution of the ruthenium(II) complex **4** was accompanied by a blueshift of the luminescence

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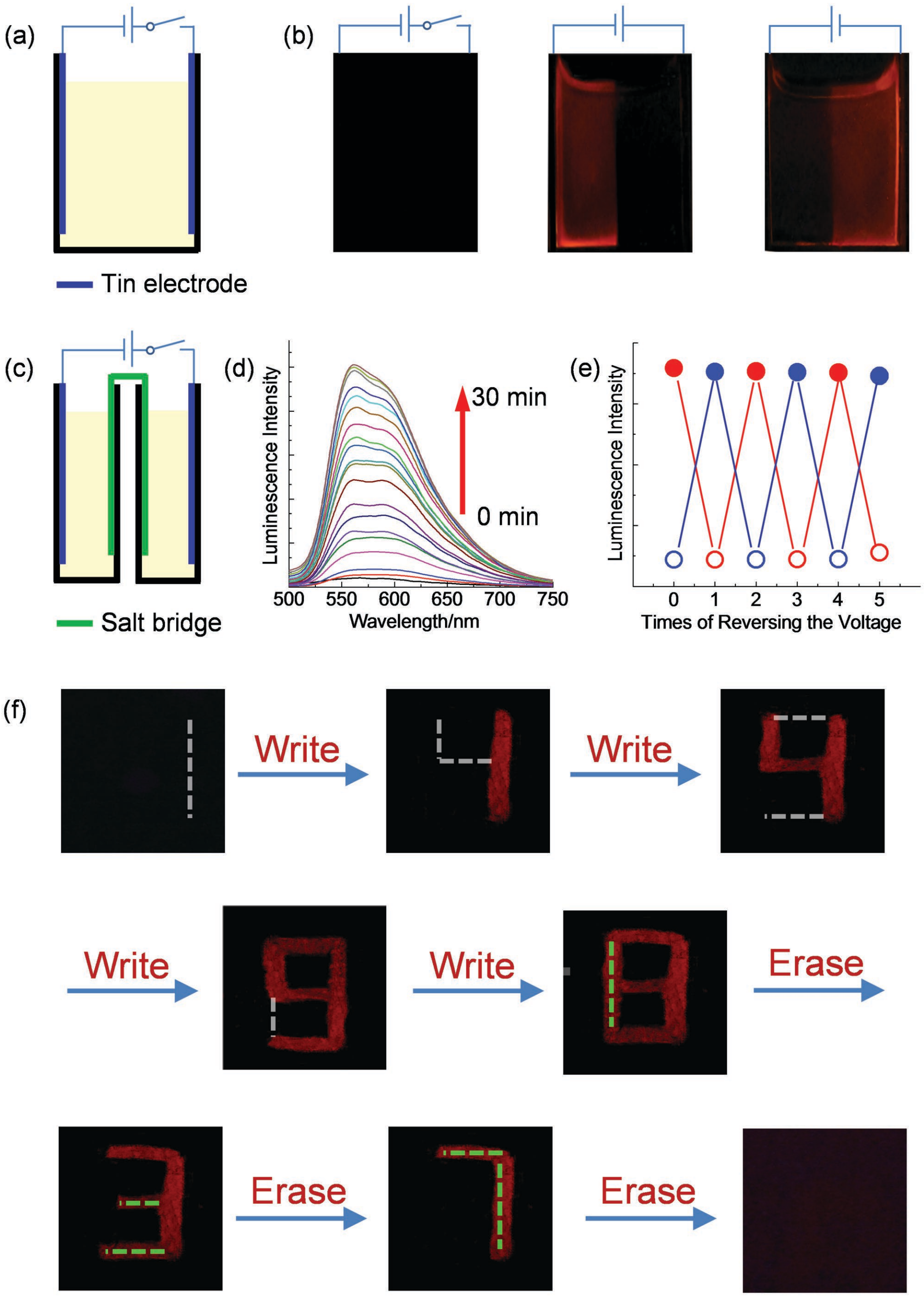

Figure 1. a) Diagram illustrating the setup for investigation of the luminescence response to an electrical stimulus. b) Photographs of complex **2** (10×10^{-6} M) in acetonitrile before (left) and after (middle) applying a voltage of 3 V, followed by reversing the voltage (right) under photoexcitation at 365 nm. c) Diagram illustrating the setup involving a salt bridge. d) Luminescence spectral trace of complex **2** (10×10^{-6} M) in acetonitrile at the cathode under an electrical stimulus for 0–30 min. e) Luminescence intensity of complex **2** (10×10^{-6} M) in acetonitrile after applying a voltage of 10 V and reversing the voltage every 5 min for 0–5 times. Solutions linked to the cathode (red) and the anode (blue) at the onset. Solutions linked to the cathode (solid) and the anode (empty) during the electrical stimulus. f) Photographs showing the stepwise writing and erasing of Arabic numerals.

maximum from 725 to 646 nm, which is in accordance with the fact that diquaternization of complex **4a** not only quenched but also redshifted the luminescence (Table S1 and Figure S3, Supporting Information). To evaluate the reversibility of the electrochromic luminescence, a voltage of 10 V was applied to the solutions of complex **2** and the direction of the voltage was changed every 5 min. In the first 5 min, the luminescence of the cathode solution was turned on. After reversing the voltage, the luminescence at the anode was quenched by 82%, while that at the cathode was enhanced by 5.5 fold. This process was repeatable and a good reversibility was observed (Figure 1e).

To demonstrate the potential applications of the methylated complexes in electrochromic luminescence devices, a quasisolid film was prepared by dissolving complex **2** in ionic liquid 1-butyl-3-methylimidazol-3-ium hexafluorophosphate (BMIM-PF_6) followed by solidification using silica. This film was mounted on an indium-tin oxide (ITO) glass which acted as an anode. Once a needle-shaped platinum cathode was used to touch the film, the luminescence turn-on was observed immediately (Figure S8, Supporting Information). Compared to the electrochromic luminescence in solution or the salt-bridge experiments, the working voltage was reduced to 1.5 V and the response time was significantly shortened because of the thinness of the film. Again, the reversibility of the electrochromic luminescence in the film was tested. When reversing the voltage direction, using the platinum anode to touch the film on the ITO cathode, the luminescence was almost-completely quenched (Figure S8, Supporting Information). The electrochromic luminescence turn-on and turn-off circles were repeated for ten times, the intensity variation of both the "on" and "off" states was less than 10% (Figure S9, Supporting Information). The utilization of this device for information recording was demonstrated. Using the platinum cathode as a "pen", a luminescent Arabic numeral "1" was written on the film (Figure 1f). Writing along the white dashed lines, numerals "4", "9", and "8" were written stepwise. After that, the voltage direction was reversed and the platinum anode worked as an "eraser". Erasing along the green dashed lines, numerals "3" and "7" and finally empty were read. The interesting electrochromic luminescence phenomenon with the advantages including good reversibility, low working voltage, and very fast response time allowed potential applications of the methylated complexes in the development of erasable electronic information recording devices.

Understanding that the electrochromic luminescence was due to reduction of the methylated moieties at the cathode, the luminescence response of complexes **1** and **2** toward different reducing agents including $NaBH_4$, NaHS, KI, and KBr has been investigated. Results showed that the complexes (10×10^{-6} M) displayed remarkable luminescence enhancement with the enhancement factors of about 22–26 and 9–10 fold upon addition of 2 equiv $NaBH_4$ and NaHS, respectively, at room temperature, while addition of KI or KBr did not cause significant luminescence changes (**Figure 2**a). The luminescence enhancement factors of complexes **1** and **2** are in line with the reducibility of these agents (BH_4^- ($\varphi o_{H_2BO_3^-/BH_4^-} = -1.24$ V) > HS^- ($\varphi o_{S/HS^-} = -0.48$ V) > I^- ($\varphi o_{I_2/I^-} = 0.54$ V) > Br^- ($\varphi o_{Br_2/Br^-} = 1.07$ V)), which suggested that the luminescence turn-on was brought about by the reduction of the pyrazinium and pyridinium moieties. Very interestingly, the reduction of both complexes by iodide was incredibly facilitated at higher temperature. As shown in Figure 2b,c, the solution of complex **2** (10×10^{-6} M) and KI (20×10^{-6} M) did not emit when the temperature was below 60 °C, but intense luminescence was observed when the temperature was increased to 75 °C. The variation in absorption spectra of the solution in the visible region at different temperatures cannot be observed due to a very low complex concentration. To investigate the effect of temperature on the redox reaction between the complex and iodide, luminescence titration of complex **2** using iodide as the titrant was performed at 25 and 75 °C, respectively. At 25 °C, complex **2** remained nonemissive when ten equivalents of iodide were added. At 75 °C, the luminescence was enhanced by 8.9 fold in the presence of the same equivalents of iodide (Figure 2d). When bromide was used instead of iodide, similar luminescence turn-on was not observed at 75 °C due to the reduced reducibility of bromide compared to iodide (Figure S10, Supporting Information). In the control experiment where the pyridine complex **2a** was used instead of the pyridinium complex **2**, the luminescence intensity remained unchanged when any of the four reducing agents was added at room temperature (Figure S11, Supporting Information). When the temperature was increased to 75 °C, complex **2a** displayed luminescence quenching due to thermally activated nonradiative decay (Figure S12, Supporting Information).

Taken together, we concluded that the methylated complexes displayed luminescence enhancement when they were chemically reduced. The reduction of the complexes by iodide was temperature-controlled. The interesting temperature-controlled iodide-induced luminescence turn-on behavior of the methylated complexes has also been observed on a thin-layer chromatography (TLC) plate. Potassium iodide solution was applied onto the right-hand side of a TLC plate and number "twelve" was written on both left- and right-hand sides of the plate using the acetonitrile solution of complex **2** as the "ink". After the TLC plate was air dried, both sides of the plate were nonemissive at room temperature under photoexcitation (Figure 2e). Interestingly, upon increasing the temperature to 75 °C, while the left "twelve" remained nonemissive, the "twelve" on the right-hand side of the plate where potassium iodide was applied exhibited bright luminescence since the reduction of pyridinium moieties by iodide was triggered at this temperature. These results demonstrated a simple information protection strategy. Compared to other information secure techniques, the use of temperature to decrypt protected information is straightforward and no special equipment is required. In this work, the decryption temperature that is higher than 60 °C (Figure 2c) is sufficiently high to avoid information leakage.

In conclusion, we incorporated pyrazinium and pyridinium moieties into transition-metal complexes and investigated their luminescence response toward electric stimuli. The complexes were nonemissive or weakly emissive due to the intramolecular oxidative quenching by the pyrazinium or pyridinium units. Upon an electrical stimulus, reduction of pyraziniums or pyridiniums of the complexes occurred at the cathode, which was accompanied by a significant photoluminescence enhancement. Owing to the good reversibility of the electrical-stimulus-induced redox conversion, the complexes have been used to develop an erasable information recording electric device. In addition, the reduction of the complexes by iodide was remarkably dependent on temperature. On the basis of this phenomenon, a new information protection device, where information can be written at room temperature but the reading of the information requires higher temperature, has been developed.

While many electrochromic materials that display remarkable changes in absorption spectra in response toward electric stimuli have been well studied, the exploration of materials that show sensitive, significant, and reversible luminescence response is still at the primary stage. Incorporation of

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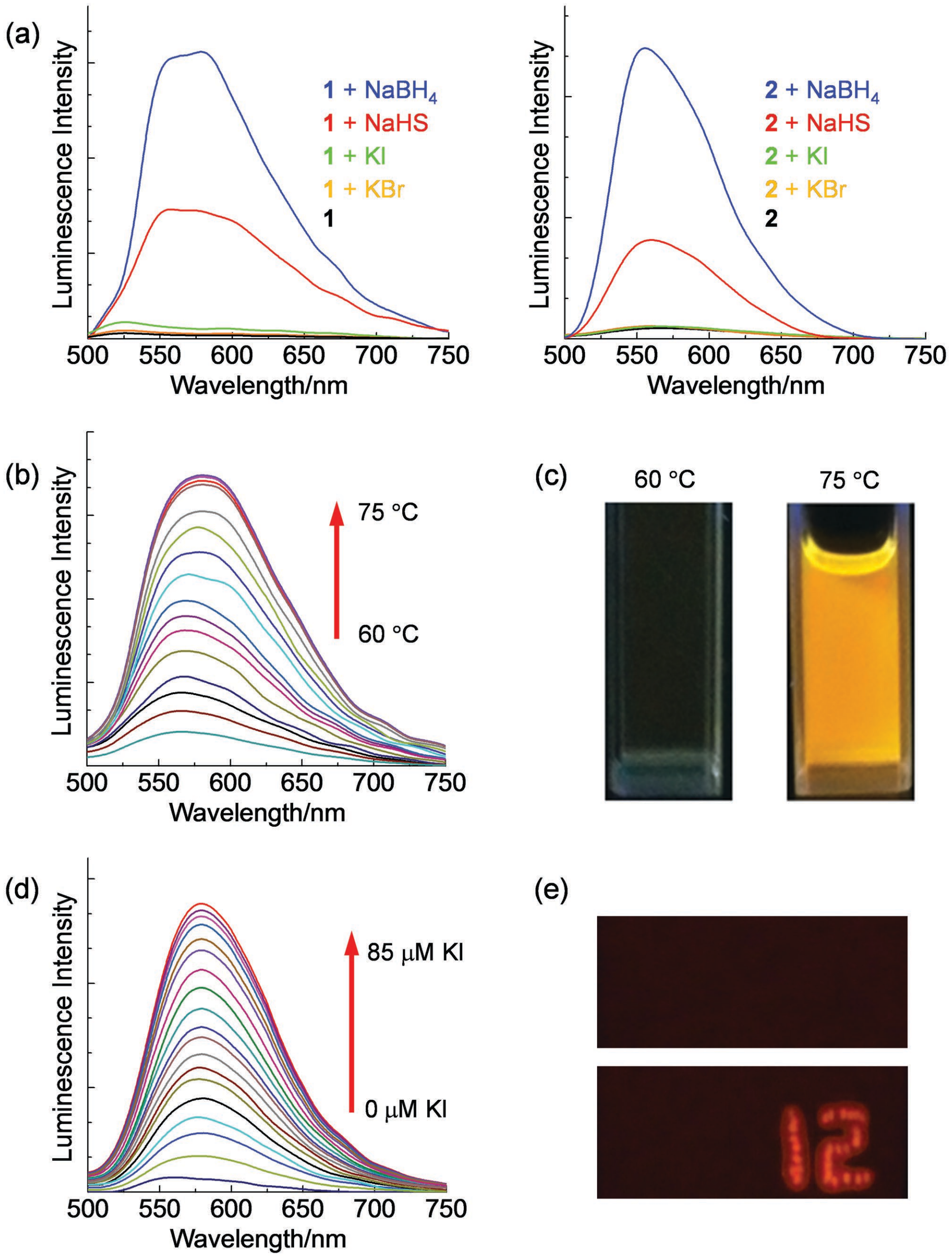

Figure 2. a) Luminescence spectra of complexes **1** (left) and **2** (right) (10×10^{-6} M) in deaerated acetonitrile in the absence (black) and presence of 2 equiv NaNH$_4$ (blue), NaHS (red), KI (green), and KBr (orange), respectively. b) Luminescence spectral trace of complex **2** (10×10^{-6} M) in deaerated acetonitrile in the presence of 2 equiv KI upon increasing temperature from 60 to 75 °C. c) Photographs of complex **2** (10×10^{-6} M) in deaerated acetonitrile in the presence of 2 equiv KI at 60 °C (left) and 75 °C (right), respectively. d) Luminescence spectral trace of complex **2** (10×10^{-6} M) in deaerated acetonitrile in the presence of 0–10 equiv KI at 75 °C. e) Photographs of the TLC plate under photoexcitation at 365 nm at 25 °C (top) and 75 °C (bottom), on which two "twelve" were written but only the right-hand side was treated with KI.

redox-active units into phosphorescent transition-metal complexes is an efficient strategy for development of electroluminochromic materials. Owing to the much higher sensitivity of electroluminochromism compared to electrochromism, we anticipate that these materials will contribute much to the development of novel and multifunctional photonic and electronic devices. Additionally, during our investigation, we unexpectedly found that reduction of these materials by iodide was temperature-dependent, which opens up a new way to develop temperature-controlled information protection strategy.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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