

Solution-Processable Electrochemiluminescent Ion Gels for Flexible, Low-Voltage, Emissive Displays on Plastic

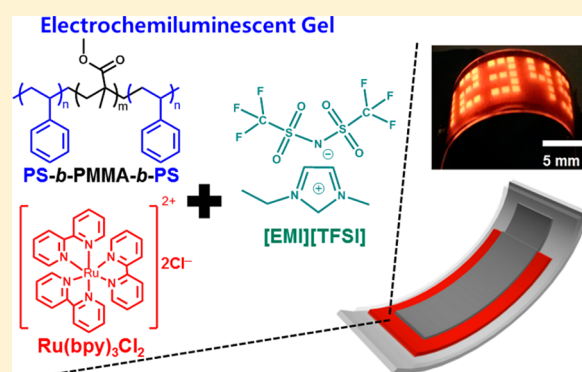
Hong Chul Moon,[†] Timothy P. Lodge,^{*,†,‡} and C. Daniel Frisbie^{*,†}

[†]Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, Minnesota 55455, United States

[‡]Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, United States

S Supporting Information

ABSTRACT: Ion gels comprising ABA triblock copolymers and ionic liquids have received much attention as functional materials in numerous applications, especially as gate dielectrics in organic transistors. Here we have expanded the functionality of ion gels by demonstrating low-voltage, flexible electrochemiluminescent (ECL) devices using patterned ion gels containing redox-active luminophores. The ECL devices consisted only of a 30 μm thick emissive gel and two electrodes and were fabricated on indium tin oxide-coated substrates (e.g., polyester) simply by solution-casting the ECL gel and brush-painting a top Ag electrode. The triblock copolymer employed in the gel was polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene, where the solvophobic polystyrene end blocks associate into micellar cross-links in the versatile ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI]). An ECL gel containing ~ 6.25 wt % $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (relative to [EMI][TFSI]) as the luminophore turned on at an AC peak-to-peak voltage as low as 2.6 V (i.e., -1.3 to $+1.3$ V) and showed a relatively rapid response (sub-ms). The wavelength of maximum emission was 610 nm (red-orange). With the use of an iridium(III) complex, $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ [diFppy = 2-(2',4'-difluorophenyl)pyridine; bpy = 2,2'-bipyridyl], the emitting color was tuned to a maximum wavelength of 540 nm (green). Moreover, when a blended luminophore system containing a 60:40 mixture of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ir}(\text{diFppy})_2(\text{bpy})^{+*}$ was used in the emissive layer, the luminance of red-orange-colored light was enhanced by a factor of 2, which is explained by the generation of the additional excited state $\text{Ru}(\text{bpy})_3^{2+*}$ by a coreactant pathway with $\text{Ir}(\text{diFppy})_2(\text{bpy})^{+*}$ in addition to the usual annihilation pathway. This is the first time that enhanced ECL has been achieved in ion gels (or ionic liquids) using a coreactant. Overall, the results indicate that ECL ion gels are attractive multifunctional materials for printed electronics.

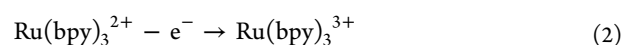
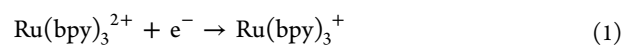


INTRODUCTION

Polymer gel electrolytes (PGEs) have found wide application in batteries,^{1,2} for example, and in healthcare for providing low-resistance electrical contacts to skin.³ Recently, PGEs have found expanding applications in flexible electronics, where they can serve as high-capacitance insulators in electrolyte-gated transistors (EGTs) and capacitors^{4–11} or as the key ion-conducting media in flexible electrochromic displays.^{12,13} A particularly promising class of PGEs are ion gels based on room-temperature ionic liquids and network-forming ABA triblock copolymers in which the A block is immiscible but the B block is miscible with the ionic liquid, giving physically cross-linked ion gels.^{4–11,14,15} On the other hand, chemically cross-linked ion gels have also been reported, in which UV irradiation through a mask or thermal cross-linking have been employed to create ion gels exhibiting both high ionic conductivity and outstanding mechanical strength.^{16–19} The notable advantages of ion gels include high ionic conductivity, high capacitance, short polarization time, negligible vapor pressure, tunable

mechanical strength, and solution processability for facile device fabrication.^{14–16}

In this article, we extend the functionality of ion gels by incorporating electrochemically emissive luminophores to produce electrochemiluminescent ion gels. Electrochemiluminescence (ECL) is light emission from an electronically excited state of a luminophore generated by an electron-transfer reaction. For example, ruthenium(II) complexes with 2,2'-bipyridyl ligands, the most well-studied luminophores for ECL, emit red-orange-colored light by an annihilation pathway. A series of reactions for tris(2,2'-bipyridyl)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$) complexes is given below:^{20,21}



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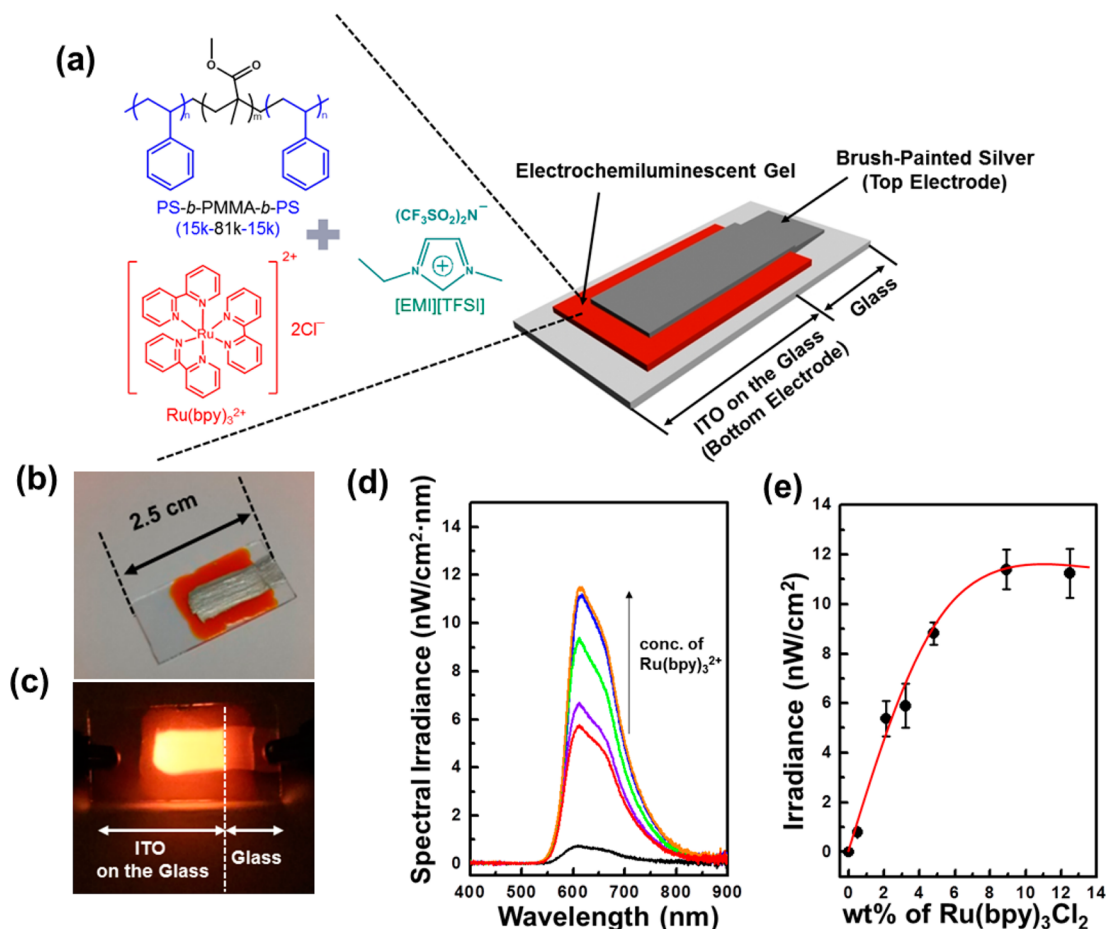
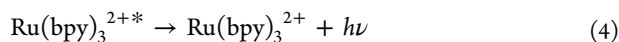
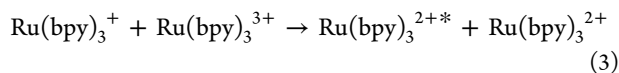


Figure 1. (a) Schematic of an ECL device with an emissive gel layer composed of $\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{PS-}b\text{-PMMA-}b\text{-PS}/[\text{EMI}][\text{TFSI}]$ in the weight ratio 1:4:16 and a brush-painted Ag electrode. (b, c) Photographs of the ECL device (b) as fabricated and (c) in the ON state, where the red-orange-colored light emission was observed from the transparent ITO side with an applied AC peak-to-peak voltage (V_{pp}) of 3.6 V (i.e., -1.8 to $+1.8$ V) at a frequency of 60 Hz. (d) Emission spectra from ECL devices with various $\text{Ru}(\text{bpy})_3\text{Cl}_2$ concentrations from 0.5 to 12.5 wt % relative to the amount of $[\text{EMI}][\text{TFSI}]$. The band at $\lambda_{\text{max}} = 610$ nm (2.04 eV) corresponds to emission of $\text{Ru}(\text{bpy})_3^{2+}$ from the $^3\text{MLCT}$ excited state. (e) Plot of the maximum irradiance at 610 nm in (d) as a function of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ concentration.



The ECL phenomenon has been studied both theoretically^{22,23} and experimentally.^{24,25} While many studies have concentrated on clarifying the working mechanism with a liquid cell composed of luminophores and supporting electrolyte solution, there have been few reports on solid-state ECL light-emitting devices.^{26–29} A potential advantage of ECL devices compared with typical organic/polymer light-emitting diodes (OLEDs/PLEDs) is their simple structure. An OLED or PLED requires multiple layers of electrodes, electron- and hole-transporting materials, and light-emissive active layers; the electronic energy levels of each layer must be tailored judiciously to facilitate charge injection and transport for efficient light emission. On the other hand, an ECL device requires only an emissive layer and two electrodes, irrespective of their work functions.

Most ECL systems reported to date are not suitable for device fabrication because of poor processability, and furthermore, previously reported solid emissive layers have displayed relatively low ionic conductivity,³⁰ resulting in long response times. Therefore, the development of a new emissive material that combines both high ionic conductivity and

mechanical strength is highly desirable in order to fabricate solid-state ECL devices. Ion gels can satisfy these criteria. Itoh^{28,29} reported gel-like emissive composites prepared by combining inorganic nanoparticles with a $\text{Ru}(\text{bpy})_3^{2+}$ -containing ionic liquid. By the addition of silica nanoparticles having a high refractive index or electrochemically active TiO_2 nanoparticles, enhanced luminescence or lower current density drops during operation, respectively, were achieved. However, when the concentration of nanoparticles was raised to increase the modulus of the composite (e.g., up to 50 wt % TiO_2 nanoparticles), the resulting materials no longer emitted light as a result of prohibitively low ionic transport.²⁹ In contrast, polymer-containing ion gels can retain high conductivity even with substantial amounts of added network-forming polymer. For example, the conductivity drop is less than a factor of 3 with 20 wt % polymer.^{31,32}

Herein we describe emissive ECL gels based on $\text{Ru}(\text{bpy})_3\text{Cl}_2$ dispersed in ion gels comprising a polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene triblock copolymer [denoted as SMS(15–81–15), where the numbers in parentheses denote the block molecular weights in kDa] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{EMI}][\text{TFSI}]$). These gels contain approximately 80 wt % $[\text{EMI}][\text{TFSI}]$. ECL devices with a simple sandwich config-

uration were fabricated on indium tin oxide (ITO)-coated substrates by solvent-casting the emissive gel and brush-painting the top Ag electrode. The devices turned on at a peak-to-peak voltage (V_{pp}) as low as 2.6 V (i.e., -1.3 to $+1.3$ V). It should be noted that an AC voltage rather than a DC voltage was applied to generate both reduced and oxidized species on the same electrode because a short diffusion length and overlapping concentration profiles for the oxidized and reduced species are essential to create an appreciable concentration of excited species and a rapid turn-ON response.^{26,27} A sub-ms response time was achieved for the ECL devices in this study. In addition, we successfully demonstrated bendable ECL devices with a patterned emissive layer on plastic substrates.

Moreover, another important requirement for an emissive display is successful color tuning of the emitted light. To this end, we synthesized 2,2'-bipyridylbis[2-(2',4'-difluorophenyl)pyridine]iridium(III) hexafluorophosphate ($\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$) to achieve green-light emission. Devices with this luminophore turned on at $V_{pp} = 3.4$ V at a frequency of 60 Hz. The ECL (and thus redox reactions) from $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (red-orange) or $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ (green) can occur simultaneously in a given voltage window. When an ECL device including both $\text{Ir}(\text{diFppy})_2(\text{bpy})^+$ and $\text{Ru}(\text{bpy})_3^{2+}$ was fabricated, red-orange-colored light was observed, and its intensity was significantly stronger than that of ECL devices containing only $\text{Ru}(\text{bpy})_3^{2+}$, presumably as a result of the formation of additional $\text{Ru}(\text{bpy})_3^{2+*}$ by a coreactant pathway. Coreactant pathways for ECL in ion gels (or ionic liquids) have not been reported previously. Overall, our results demonstrate a promising approach to light-emitting PGEs and their incorporation into easily fabricated, low voltage, emissive displays on plastic.

RESULTS AND DISCUSSION

Fabrication and Characterization of ECL Devices.

Figure 1a shows a schematic diagram of the ECL device. $\text{Ru}(\text{bpy})_3\text{Cl}_2$, SMS(15–81–15), and $[\text{EMI}][\text{TFSI}]$ were mixed to prepare ECL gels in weight ratios of 1:4:16, in which the PMMA domain is swollen by $\text{Ru}(\text{bpy})_3^{2+}$ -containing $[\text{EMI}][\text{TFSI}]$. It should be noted that this particular ECL gel was so soft that physical vapor deposition of the top electrode onto the ECL gel was difficult. Therefore, we employed brush-painted Ag for the top electrode, following ref 33, where a PLED with a brush-painted Ag cathode worked successfully and performed comparably to that with a thermally deposited Ag electrode. Accordingly, the ECL device was fabricated by a simple two-step solution process. The ECL gel was prepared on the ITO-coated substrate in one step by solution-casting from a single ethyl acetate solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$, SMS(15–81–15), and $[\text{EMI}][\text{TFSI}]$, after which the Ag electrode was deposited using brush-painting of Ag paint. Figure 1b,c displays ECL devices on patterned ITO-coated glass as fabricated and in the ON state, respectively. Light emission with $\lambda_{\text{max}} = 610$ nm (2.04 eV) (Figure 1d), corresponding to the transition of $\text{Ru}(\text{bpy})_3^{2+}$ from the triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) excited state to the ground state,³⁴ was observed exclusively within the area sandwiched between ITO and the Ag electrode (see Figure 1c). Thus, once the top electrode was painted on the ECL gel, light emissive patterns with arbitrary shapes could be prepared. Indeed, we successfully demonstrated emissive lines and letters based on this concept (see Figure S1 in the Supporting Information). The ECL intensity was enhanced as the concentration of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was increased, as shown in

Figure 1d. Figure 1e is a plot of maximum irradiance from Figure 1d versus concentration of $\text{Ru}(\text{bpy})_3\text{Cl}_2$. The irradiance first increased with $\text{Ru}(\text{bpy})_3\text{Cl}_2$ concentration before saturating at about 9 wt % relative to the amount of $[\text{EMI}][\text{TFSI}]$, which is consistent with previous results obtained from a $\text{Ru}(\text{bpy})_3^{2+}$ -containing electrochemical liquid cell.^{35,36}

Dependence of ECL on Applied Frequency and Voltage. To investigate the relationship between the ECL luminance and the applied voltage, we performed AC voltage sweeps at various frequencies (Figure 2). At a frequency of 60

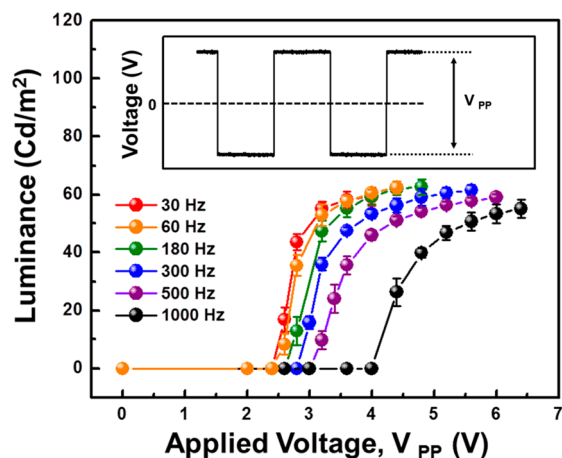


Figure 2. Dependence of the peak luminance on the applied voltage at AC input frequencies from 30 to 1000 Hz.

Hz, the ECL device emitted light at V_{pp} as low as 2.6 V (-1.3 to $+1.3$ V), and the luminance saturated at ~ 4.0 V. As the applied frequency increased, we observed decreasing luminance at a fixed voltage. This behavior can have several origins, including gel ionic resistance (voltage drop) and reaction/mass transport dynamics near the electrodes.^{22,23} For example, higher-frequency switching can lead to higher transient ionic currents and larger resistive voltage drops in the gel, which impact the redox reactions at the electrode surface. A similar frequency dependence of the ECL intensity has been reported in the ECL systems of thianthrene/2,5-diphenyl-1,3,4-oxadiazole,³⁷ 5-amino-1,2,3,4-tetrahydrophthalazine-1,4-dione (luminol),³⁸ and 10-methylphenothiazine.³⁹ The point of Figure 2 is that the frequency and the necessary applied voltage are intimately related, which is important for device applications.

Dynamics of the ECL Devices. To investigate the transient behavior of the ECL devices, the applied voltage, current, and ECL intensity were recorded as functions of time (Figure 3a). A square-wave voltage oscillating from -1.8 to $+1.8$ V at a frequency of 60 Hz was applied. The emission delay time was determined to be sub-ms by measuring the time difference between the positive and negative switching of the applied voltage and ECL emission, as shown in Figure 3b,c, respectively. This delay time is much longer than the RC polarization time constant ($30 \mu\text{s}$) for ECL gels in this study.⁴⁰ Thus, the delay likely does not originate from the formation of electrical double layers (EDLs). According to both theoretical²³ and experimental²⁶ studies, the emission delay corresponds to the requisite time for the regeneration of $\text{Ru}(\text{bpy})_3^{2+}$ and the diffusion of redox species [$\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$] to meet, which is described in more detail as follows.

A schematic illustration of these reactions near the electrode surface when the applied voltage switches from negative to

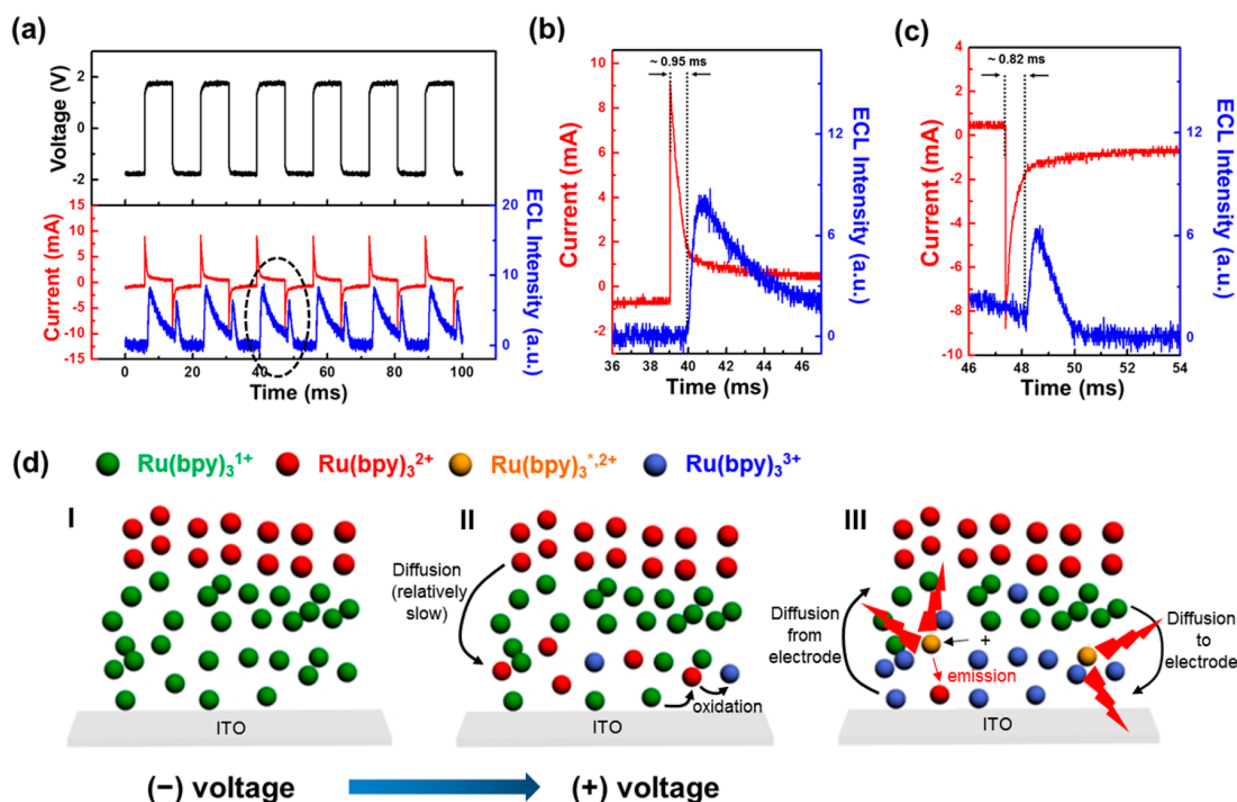
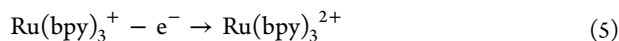


Figure 3. (a) Dynamic profiles of applied voltage ($V_{pp} = 3.6$ V, square wave) (black), current (red), and ECL intensity (blue) for the ECL device at a frequency of 60 Hz. (b, c) Enlargements of the area circled in (a) that show the voltage switching (b) from negative to positive and (c) from positive to negative. (d) Schematic showing chemical species and reactions near the electrode when the voltage switches from negative to positive.

positive is given in Figure 3d. First the $\text{Ru}(\text{bpy})_3^{2+}$ regeneration reaction shown in eq 5 occurs near the electrode surface because of the high concentration of $\text{Ru}(\text{bpy})_3^+$:



Simultaneously, the low concentration of $\text{Ru}(\text{bpy})_3^{2+}$ near the electrode causes diffusion of $\text{Ru}(\text{bpy})_3^{2+}$ from the bulk to the electrode surface (stage II in Figure 3d). Since this diffusion is a relatively slow process, the main source for $\text{Ru}(\text{bpy})_3^{2+}$ in the early stage is the regeneration reaction (eq 5) rather than the supply from the bulk by diffusion.^{20,23} The regenerated (or supplied) $\text{Ru}(\text{bpy})_3^{2+}$ is then oxidized further to $\text{Ru}(\text{bpy})_3^{3+}$. Accordingly, $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(\text{bpy})_3^{3+}$ diffuse toward the electrode and the bulk, respectively, because of the resulting concentration gradients. When the concentration profiles of $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(\text{bpy})_3^{3+}$ overlap, the electron-transfer reaction occurs to form excited $\text{Ru}(\text{bpy})_3^{2+*}$, which emits light by ECL (stage III in Figure 3d). When the applied frequency was varied, the transient profiles for applied voltage, current, and ECL signal were very similar to those at 60 Hz, with the exception of the response emission (which had a somewhat shorter response time at a higher frequency; see Figure S2 in the Supporting Information).

Fabrication of Patterned Flexible ECL Devices. The significant advantages of the ECL gel are good mechanical strength, enabling the fabrication of flexible solid-state devices, and solution processability, allowing for facile device fabrication. To take advantage of such features, we fabricated bendable ECL devices on plastic with patterned gels following the procedure illustrated in Figure 4a. Although we have already demonstrated ECL devices that emit light using brush-

painted silver electrodes (e.g., Figure 1c), in this case negative photoresist (SU-8) patterns were prepared by photolithography to define the shape and size of the emissive area more precisely.

The patterned nonconductive photoresist on the substrate acted as a spacer (thickness: 10 μm) as well as a template. After preparation of the photoresist pattern, device fabrication was completed by sequential deposition of the ECL gel and Ag electrode by solution-casting and brush-painting, respectively. Indeed, the fabricated devices emitted light only within the patterned areas. The ECL devices with patterns of numbers composed of tiny squares worked successfully even after bending (Figure 4b), which demonstrates the potential for ECL devices as simple, flexible emissive displays.

Color-Tuning of the Emitted Light from an ECL Device. Color-tuning of the emitted light from an ECL device is another challenge for a successful emissive display. For this purpose, we synthesized $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ as an ECL luminophore for green-colored light. The synthetic route is given in Scheme 1.^{41,42} Similar to $\text{Ru}(\text{bpy})_3\text{Cl}_2$, $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ has good solubility in various organic solvents such as ethyl acetate, the cosolvent for the preparation of ECL gels, and thus, an ECL device emitting green-colored light could be prepared easily. A wavelength maximum of 540 nm (2.30 eV), corresponding to a green color, was observed in the emission spectrum for an ECL device containing $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ (Figure 5a). To investigate the dependence of the luminance on the $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ concentration, the amount of $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ in the ECL gel was varied. The weight percentage of $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ was calculated versus the amount of $[\text{EMI}][\text{TFSI}]$. The luminance increased with increasing $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ concentration

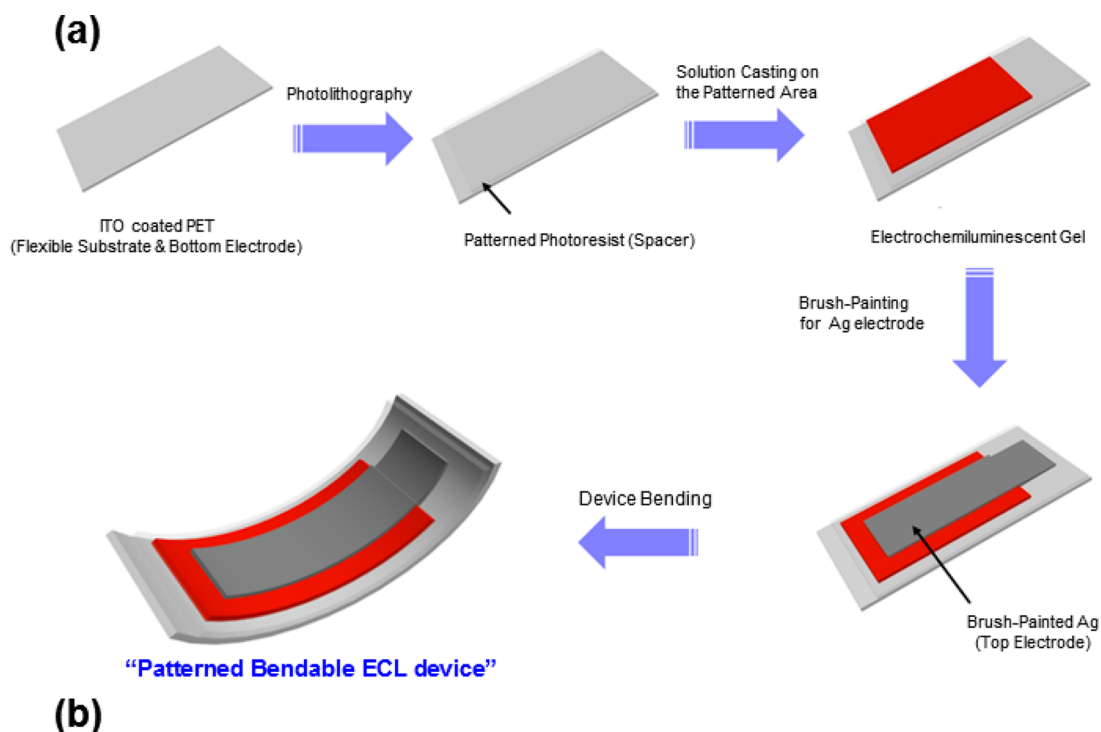
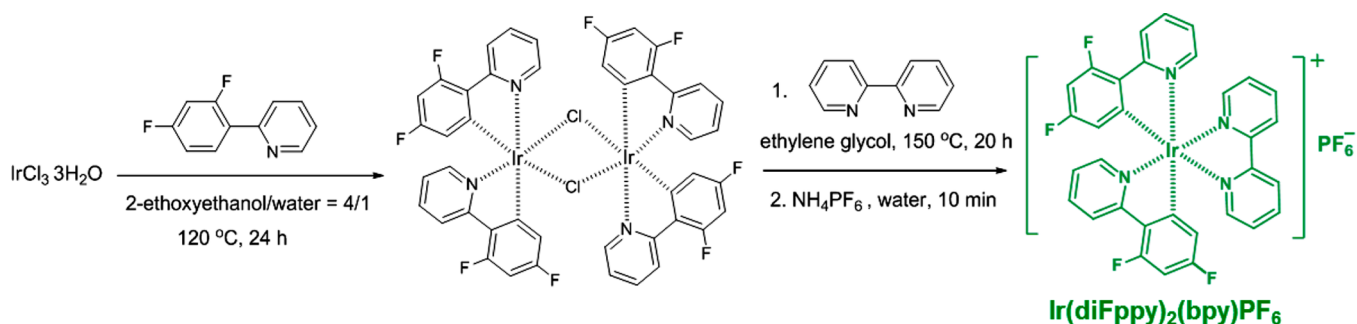


Figure 4. (a) Schematic of the fabrication process for bendable ECL devices with patterned ECL gels on plastic. (b) Photographs of the ON states for fabricated ECL devices before bending (left image) and after bending (right image), where the applied voltage and frequency were $V_{pp} = 3.6$ V (−1.8 to +1.8 V) and 60 Hz, respectively. The Arabic numerals are composed of 1 mm × 1 mm squares.

Scheme 1. Synthetic Route To Prepare $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$



until it reached saturation when the concentration of $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ exceeded ~ 8 wt % (Figure 5b). Also, sweeps of applied voltage were used to determine the turn-ON voltage for a green-emission ECL device having 8 wt % $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$. The ECL device turned ON at $V_{pp} = 3.4$, and its luminance reached a maximum at $V_{pp} \approx 4.0$ (Figure 5c). It should be noted that the turn-ON voltage for the $\text{Ir}(\text{diFppy})_2(\text{bpy})^+$ -containing ECL device ($V_{pp} = 3.4$ V) is slightly larger than that for the $\text{Ru}(\text{bpy})_3^{2+}$ -containing system ($V_{pp} = 2.6$ V). This is reasonable because $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ has a larger oxidation potential of +1.23 V and a more negative

reduction potential of -1.34 V (i.e., a larger HOMO–LUMO gap) compared with $\text{Ru}(\text{bpy})_3\text{Cl}_2$, as determined by cyclic voltammetry (see Figure S3 in the Supporting Information).

Enhancement of the ECL Intensity. Very interestingly, when we prepared ECL devices having both $\text{Ir}(\text{diFppy})_2(\text{bpy})^+$ and $\text{Ru}(\text{bpy})_3^{2+}$, an enhancement of the luminance was achieved. Figure 6a shows the spectra for ECL devices containing different $\text{Ir}(\text{diFppy})_2(\text{bpy})^+:\text{Ru}(\text{bpy})_3^{2+}$ mole ratios with a fixed total amount of luminophores (11.4 μmol). In contrast to a previous report where two distinct ECL spectra from $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ir}(\text{ppy})_3$ were observed simultaneously,⁴³

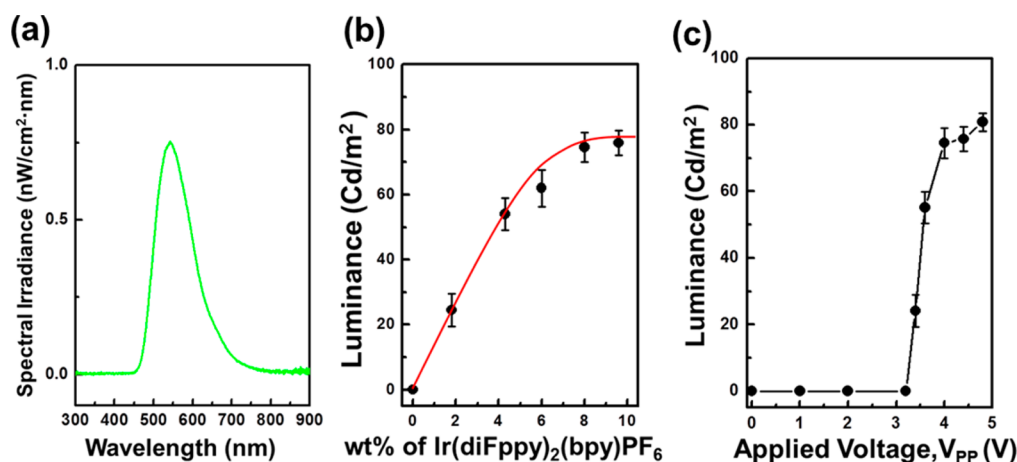


Figure 5. (a) Emission spectrum with $\lambda_{\text{max}} = 540$ nm from an ECL device containing $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$. (b) Dependence of the luminance on the $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ concentration relative to $[\text{EMI}][\text{TFSI}]$ in an ECL gel at $V_{\text{PP}} = 4.0$ V and a frequency of 60 Hz. (c) Luminance vs applied voltage for an ECL device containing 8 wt % $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ at a frequency of 60 Hz.

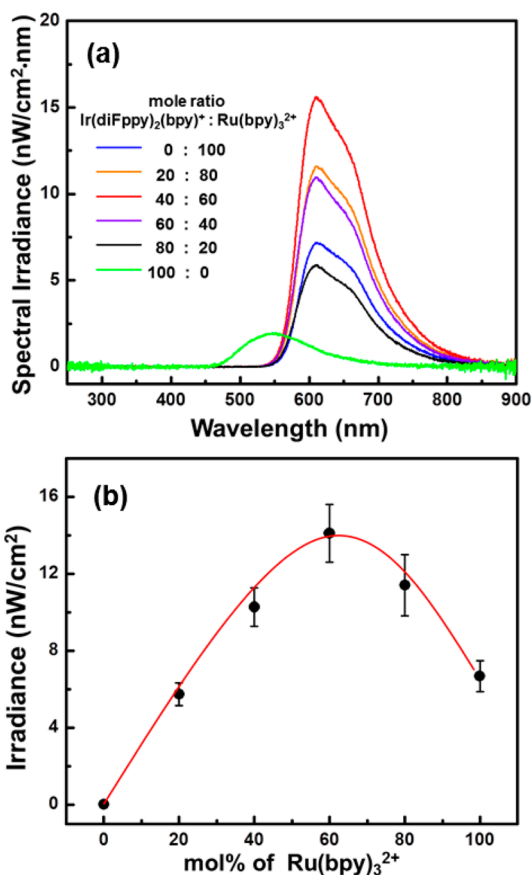


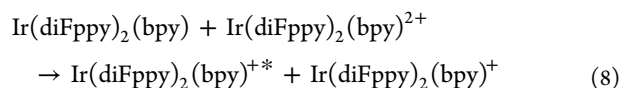
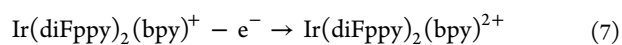
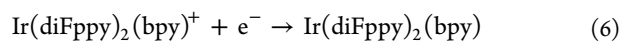
Figure 6. (a) Change in the ECL spectrum as the $\text{Ir}(\text{diFppy})_2(\text{bpy})^+:\text{Ru}(\text{bpy})_3^{2+}$ mole ratio was varied at a fixed total amount of luminophores $[\text{Ir}(\text{diFppy})_2(\text{bpy})^+ + \text{Ru}(\text{bpy})_3^{2+}] = 11.4$ μmol . (b) Plot of irradiance at $\lambda = 610$ nm vs mole percent of $\text{Ru}(\text{bpy})_3^{2+}$ in the $\text{Ir}(\text{diFppy})_2(\text{bpy})^+ + \text{Ru}(\text{bpy})_3^{2+}$ mixture.

when $\text{Ru}(\text{bpy})_3^{2+}$ was added to $\text{Ir}(\text{diFppy})_2(\text{bpy})^+$, the ECL spectrum from $\text{Ir}(\text{diFppy})_2(\text{bpy})^+$ was diminished remarkably and a strong ECL spectrum corresponding to that arising from $\text{Ru}(\text{bpy})_3^{2+}$ was observed. As the concentration of $\text{Ru}(\text{bpy})_3^{2+}$ was increased from 0 to 60 mol %, the intensity of the red-orange-colored light was enhanced continuously. However, above 60 mol % $\text{Ru}(\text{bpy})_3^{2+}$, the ECL signal dropped again.

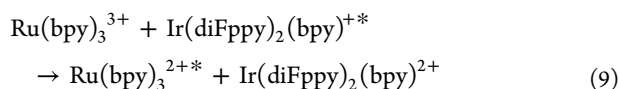
Figure 6b displays a plot of irradiance at 610 nm as a function of the mole percent of $\text{Ru}(\text{bpy})_3^{2+}$ in the $\text{Ir}(\text{diFppy})_2(\text{bpy})^+ + \text{Ru}(\text{bpy})_3^{2+}$ mixture. In this blended luminophore system, a maximum irradiance was achieved near 60 mol % $\text{Ru}(\text{bpy})_3^{2+}$.

One possible reason for the enhanced intensity of the red-orange-colored light is resonance energy transfer between $\text{Ir}(\text{III})$ and $\text{Ru}(\text{II})$ complexes. In this case, however, the resonance energy transfer is likely to be small because of the limited overlap between the absorption spectrum of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and the emission spectrum of $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ (see Figure S4 in the Supporting Information). Moreover, when we recorded the emission spectra for a blended luminophore system, all of the spectra with a $\text{Ru}(\text{bpy})_3^{2+}$ composition from 20 to 80 wt % corresponded to red-orange-colored light, without any peak associated with the green-colored light from $\text{Ir}(\text{diFppy})_2(\text{bpy})\text{PF}_6$ (see Figure 6a). This result also implies that the higher intensity of the mixed luminophore system is attributable to other reasons.⁴⁴

Recently, Doeven et al.⁴⁴ reported the selective excitation of mixed luminophores by controlling an electrode potential. When they selected two ECL luminophores, the green emitter $\text{Ir}(\text{ppy})_3$ ($\text{ppy} = 2\text{-phenylpyridine}$) and the red emitter $\text{Ru}(\text{bpy})_2\text{L}^{2+}$ [$\text{L} = \text{N}^4, \text{N}^{4'}\text{-bis}((2\text{S})\text{-1-methoxy-1-oxopropan-2-yl})\text{-2,2'-bipyridyl-4,4'-dicarboxamide}$], only red emission was observed at a high potential. It should be noted that they used one of the well-known coreactants, tri-*n*-propylamine (TPA).^{20,45} As a result, $\text{Ir}(\text{ppy})_3^*$ emitting green-colored light was quenched oxidatively by the TPA radical cations. On the other hand, we did not employ any coreactant, and thus, only redox species associated with $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ir}(\text{diFppy})_2(\text{bpy})^+$ were present. According to the literature, $\text{Ir}(\text{III})$ complexes in the excited state can be potent reducing agents because of their high triplet-state energies.^{46,47} Therefore, excited $\text{Ir}(\text{diFppy})_2(\text{bpy})^{+*}$ could be generated by the series of reactions shown in eqs 6–8,



and could then act as a reducing agent similar to TPA. Indeed, Ir(III) complexes have been employed to serve as photoactive catalysts and reducing agents.^{48,49} Therefore, one possible way to produce Ru(bpy)₃^{2+*} would be an electron-transfer reaction between Ru(bpy)₃³⁺ and Ir(diFppy)₂(bpy)^{+*} instead of TPA,^{20,45} as shown in eq 9:



Therefore, with the additional formation of Ru(bpy)₃^{2+*} by a coreactant pathway with Ir(diFppy)₂(bpy)^{+*} (eqs 6–9), the overall amount of Ru(bpy)₃^{2+*} in the blended luminophore system is larger than that in the Ru(bpy)₃Cl₂-only system, where the general annihilation pathway (eqs 1–4) is the only route to form Ru(bpy)₃^{2+*}. As a result, the ECL intensity of red-orange-colored light is doubled in the blended luminophore system. It is noteworthy that the excited Ir(III) complex [here, Ir(diFppy)₂(bpy)^{+*}] is available as a coreactant for the ECL system. While most well-known coreactants, such as TPA,^{20,45} peroxydisulfate (S₂O₈²⁻),^{50,51} oxalate ion (C₂O₄²⁻),⁵² and benzoyl peroxide,⁵³ have very limited solubility in ionic liquids or organic solvents, Ir(diFppy)₂(bpy)^{+*} is highly soluble in both of them, providing an opportunity to investigate ECL with a coreactant pathway in various media.

For direct comparison of luminance, we fabricated devices based on ECL gels with three different luminophore systems: Ir(diFppy)₂(bpy)⁺ only, Ir(diFppy)₂(bpy)⁺ + Ru(bpy)₃²⁺ with the optimized Ru(bpy)₃²⁺:Ir(diFppy)₂(bpy)⁺ mole ratio of 60:40, and Ru(bpy)₃²⁺ only. A scheme and a photograph of the fabricated ECL devices on the same patterned ITO-coated glass substrate are given in Figure 7a,b, respectively. The three ECL

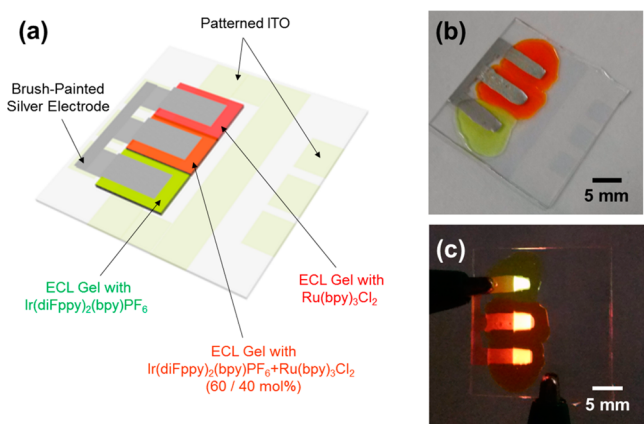


Figure 7. (a) Schematic of three ECL devices with different luminophore systems: Ir(diFppy)₂(bpy)⁺ only, 40 mol % Ir(diFppy)₂(bpy)⁺ + 60 mol % Ru(bpy)₃²⁺, and Ru(bpy)₃²⁺ only. (B, c) Photographs of the fabricated three ECL devices (b) as fabricated and (c) in the ON state at $V_{pp} = 4.0$ V and a frequency of 60 Hz.

devices were connected by Ag paste to turn on at the same time. All three ECL devices turned on simultaneously when a V_{pp} of 4.0 V at a frequency of 60 Hz was applied (Figure 7c). Visual observation clearly confirmed the enhanced luminance for the ECL device with blended luminophores (middle device in Figure 7c) compared with that for the Ru(bpy)₃²⁺ only device (bottom in Figure 7c), even though both devices contained the same amount of Ru(bpy)₃²⁺ in the gel.

SUMMARY

The novelty of this work lies in (1) the first demonstration of a block-copolymer-based emissive ion gel, (2) the low-voltage operation ($V_{pp} = 2.6$ V, i.e., -1.3 to $+1.3$ V) and quick response time (sub-ms) of the fabricated ECL devices, (3) the successful demonstration of flexible emissive devices with various patterns, (4) the achievement of color tuning for ECL devices by employing another luminophore, and (5) the discovery and utilization of Ir(diFppy)₂(bpy)^{+*} as a coreactant that yields a remarkable luminance enhancement of red-orange-colored light-emitting ECL devices by a coreactant pathway in addition to the usual annihilation pathway.

Although the ECL gel in this work opens up the opportunity for the fabrication of solid-state emissive ECL devices, there are still many remaining issues to address. For instance, while we applied an AC voltage to achieve overlapping concentration profiles of luminophores, DC operation may be preferred to integrate ECL devices into circuits. However, DC operation with the annihilation pathway has drawbacks such as a longer turn-ON time and lower brightness than AC operation.⁵⁴ The incorporation of a coreactant into the ECL gels or the fabrication of very thin ECL devices to reduce the diffusion length of redox species from each electrode would be one possible solution. Ultimately, this simple but effective rubbery ECL gel could be attractive for flexible electronics applications such as displays on packaging or wearable luminescent safety tags.

EXPERIMENTAL SECTION

Materials. All of the chemicals, including tris(2,2'-bipyridyl)-dichlororuthenium(II) hexahydrate (Ru(bpy)₃Cl₂), were purchased from Sigma-Aldrich and used as received. 2,2'-Bipyridylbis[2-(2',4'-difluorophenyl)pyridine]iridium(III) hexafluorophosphate (Ir(diFppy)₂(bpy)PF₆) was synthesized via a two-step reaction following the literature.^{41,42} The polystyrene-*block*-poly(methyl methacrylate)-*block*-polystyrene triblock copolymer [SMS(15–81–15)] and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI]) were prepared by two-step atom-transfer radical polymerization (ATRP)³¹ and an anion exchange reaction,⁵⁵ respectively. ITO-coated glass (sheet resistance 8–12 Ω/sq, Delta Technologies Ltd.) and ITO-coated PET film (sheet resistance 60 Ω/sq, Sigma-Aldrich) were sequentially rinsed with acetone (5 min), methanol (5 min), and isopropanol (5 min) under sonication and then subjected to UV/ozone treatment for 10 min before use.

Preparation of Patterned Photoresists. Photoresist patterns with desired shapes were fabricated using photolithography. First, the photoresist (SU-8 2010, Micro Chem) was spin-coated onto the ITO-coated substrate (glass or PET film) at 3000 rpm for 60 s. After soft baking at 95 °C for 3 min, the photoresist film was exposed to UV light (MA6, Karl Suss) for 12 s with a mask. The exposed film was then baked at 95 °C for 3 min, followed by rinsing with developer for 3 min. Finally, the film was cured at 150 °C for 15 min.

ECL Device Fabrication and Characterization. ECL devices with the simple structure of ITO/ECL gel/Ag were fabricated in ambient air. An ECL gel with a thickness of ~30 μm as determined with a digital microscope (KH-7700, Hirox-USA Inc.) was prepared on the patterned photoresist using solution-casting from an ethyl acetate solution of Ru(bpy)₃Cl₂/SMS(15–81–15)/[EMI][TFSI] (1.4:16 w/w/w). The cast ECL film was dried at 30 °C for 24 h, and residual solvent was removed fully under reduced pressure. The Ag electrode was then deposited by brush-painting of Ag paint. The spectrum of emitted light from the ECL gel was recorded on an Ocean Optics HR4000 spectrometer. The luminance of the ECL device was estimated using a Hamamatsu S3584-08 photodetector, whereas transient profiles of the ECL signals were obtained with a smaller photodetector (PDA36A, Thorlabs). Also, transient profiles of the

applied AC voltage generated by an arbitrary waveform generator (33220A, Agilent) and the current were recorded on an oscilloscope (TDS1002B, Tektronix). All of the measurements were performed in ambient air.

■ ASSOCIATED CONTENT

■ Supporting Information

Demonstration of brush-painted silver as a top electrode for ECL devices, transient profiles at different frequencies for Ru(bpy)₃Cl₂-containing ECL devices, cyclic voltammetry results for Ru(bpy)₃Cl₂ and Ir(diFppy)₂(bpy)PF₆, and the UV-vis spectrum (absorption) of Ru(bpy)₃Cl₂ and ECL spectrum (emission) of Ir(diFppy)₂(bpy)PF₆. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

lodge@umn.edu

frisbie@umn.edu

Notes

The authors declare no competing financial interest.

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