New Approach Toward Fast Response Light-Emitting Electrochemical Cells Based on Neutral Iridium Complexes via Cation Transport

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Here, a new method is presented to increase the turn-on time and stability of light-emitting electrochemical cells (LECs). To this end, a neutral iridium complex (5) containing a pendant Na^+ ion that is generally known to have a faster mobility in the solid film than bulky anions is introduced, instead of the classic ionic transition metal complex (iTMC) with counter anion (7). Synthesis, photophysical and electrochemical studies of these complexes are reported. In the device configuration of ITO/5 or 7+PEO (polyethylene oxide) (100–110 nm)/Au, as the voltage increases, complex 5 emits red light at -3.6 V while complex 7 appears at -5.6 V, although their electrochemical and photophysical gap are similar. Furthermore, at constant voltage, -3 V, the turn-on time of complex 5 was less than 0.5 min, which is a 60-fold faster turn-on time compared to the iTMC (7) with PF_6^-. These results are presumably due to the faster delivery of the Na^+ ions to the electrode compared to PF_6^- ions. Also, the device lifetime of complex 5 exhibits a six-fold increase in stability and a three-fold shorter time to reach maximum brightness at constant bias compared to the device made with complex 7.

1. Introduction

Light-emitting electrochemical cells (LECs) have attracted much attention as promising alternatives for organic light-emitting diodes (OLEDs).[1–11] The major difference between LECs and OLEDs[12–14] is that the operational mechanism of LECs is dominated by the presence of mobile ions in a single layer, while that of OLEDs depends on the migration of excitons in a multilayer. Due to the intrinsic mechanism involving ion transport, LECs offer several advantages over OLEDs, such as low turn-on voltage, simple fabrication, and they can be used with air-stable electrodes. Upon application of a bias in LECs, the counterions associated with the complexes are redistributed in the vicinity of the electrodes. This charge redistribution produces high electric

fields at the electrode interfaces and enhances the injection of holes and electrons at the anode and cathode, respectively.

Until now, several different types of LECs have been developed since conjugated polymers, MEH-PPV (poly[5-(2′-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene]) blended with PEO (polyethyleneoxide), was reported.[1] For example, single-layer LECs based on ionic transition metal complexes (iTMCs)[3–11] have been reported because they show several advantages over conventional polymer LECs, such as good thermal stabilities and charge transport properties.[5] Due to these advantages, various cationic ruthenium,[2–4] osmium(I),[5] and Re(I) complexes,[6] balanced by a large negative counterion such as PF_6^-, have been developed. More recently, ionic iridium complexes have attracted more attention.[7–9] Because they have a great potential to offer not only high quantum yield but high ligand field strength,[9a] they can be easy to control the emitted color, through the change of main and/or ancillary ligands with high efficiency. However, although these complexes show high efficiency with various colors, slow response time is not yet solved.

2. Results and Discussion

Although the use of LECs offers considerable advantages, LECs still suffer from several serious problems that need to be solved before they can be commercialized. For instance, since their turn-on time is dependent on the mobility of the counterions, it usually ranges from a few seconds to several hours. In order for an LEC to be of practical use, its turn-on time must be less than a few milliseconds. A number of studies have focused on the improvement of the turn-on times of iTMC-based LECs.[3,7b] Changing the counterion of an iTMC is one known method for reducing the turn-on time. For instance, decreasing the size of the counterions by replacing PF_6^- with ClO_4^- or BF_4^- has been found to reduce the turn-on time from several minutes to a few seconds.[3c,d,7b] Due to the facile transport of cations under the influence of the external bias, the polymer LEC involving cation diffusion shows a relatively fast response time.[15] It is known that

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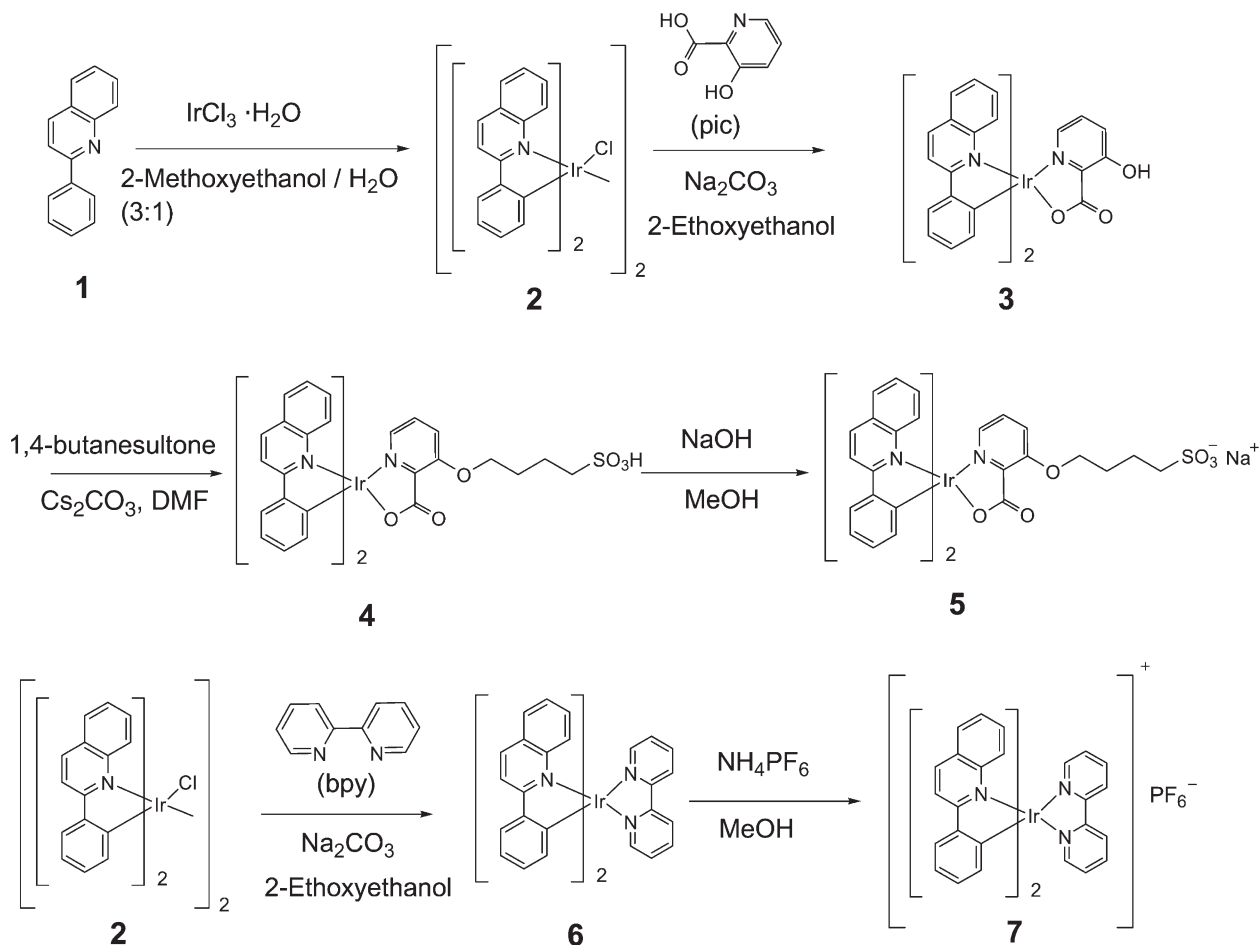
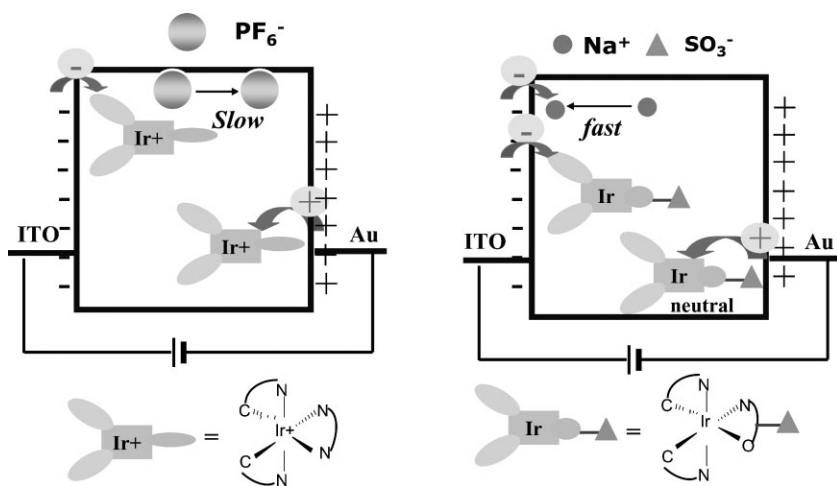**Scheme 1.** Synthesis of Complexes **5** and **7**.

Figure 1. Schematic distribution of the ionic species in an ionic Ir complex (**7**, left) and a neutral Ir complex (**5**, right), respectively, under reverse bias.

the nature of the ion does not only affect the turn-on time, it also influences device stability.[3–11]

To overcome the slow turn-on times associated with iTMC-based LECs, we suggest the use of a neutral Ir(III) complex (**5**) with a pendant counter cation instead of a cationic iridium complex (**7**) with a PF_6^- counter anion. In this study, a neutral iridium complex (**5**) with a pendant sodium ion was prepared, along with a cationic iridium complex (**7**) with a PF_6^- counter anion as a reference (Scheme 1). Figure 1 illustrates the advantage of using complex **5** instead of complex **7**. Under reverse bias, the Na^+ in the neutral Ir(III) complex would move relatively fast to the ITO electrode, while the PF_6^- in the ionic Ir(III) complex would diffuse relatively slowly to the metal electrode. Therefore, we expect complex **5**

to result in a faster response speed than complex **7** with a big size counter anion (PF_6^-).

2.1. Synthesis

In this study, 2-phenylquinoline (pq, **1**) was chosen as the main ligand in the iridium complexes because a previously reported iridium complex based on iridium(III) bis(2-phenylquinolato-$N,C^{2'}$)picolinate exhibited reversible electrochemical behavior ($i_{pc}/i_{pa} = 0.92$, $i_{pa}/i_{pc} = 0.92$) and a high yield of electrogenerated chemiluminescence (ECL) ($\phi_{ECL} = 0.88$) upon pulsed voltammetry.[16] To make a reference ionic iridium complex, bipyridine and PF_6^- were chosen as the ancillary ligand and counter anion, respectively.

Scheme 1 illustrates the synthesis of the new compounds examined in this study. Ir(III) dimers were synthesized using the method reported by Nonoyama.[17] A mixture of the chloro-bridged dimer (**2**), 3-hydroxypicolinic acid, and sodium carbonate was refluxed in an inert atmosphere in 2-ethoxyethanol to yield complex **3**. Complex **3** was reacted with 1,4-butanesultone in the presence of cesium carbonate in N,N'-dimethylformamide (DMF) to produce complex **4**. Complex **4** was treated with NaOH in methanol to obtain complex **5**. A mixture of complex **2** and bipyridine (bpy) was refluxed in 2-ethoxyethanol to furnish complex **6**, which was then treated with NH_4PF_6 in methanol to yield complex **7**.

2.2. Photophysical and Electrochemical Properties

2.2.1. Photophysical Studies

The photophysical properties of complexes **5** and **7** are presented in Table 1 and Figure 2. The absorption spectrum of each compounds in 2-methyltetrahydrofuran (2-MeTHF) shows an intense band ($\varepsilon > 10^4 \, M^{-1} \, cm^{-1}$) in the ultraviolet part of the spectrum between 250 and 300 nm. These bands are assigned to the spin-allowed $^1\pi-\pi^*$ ligand-centered (LC) transition in both the $C^\wedge N$ and $N^\wedge N$ ligands (Fig. 1). The low energy absorption features in the 300 and 500 nm range are associated with both spin-allowed and spin-forbidden metal-to-ligand charge transfer (MLCT) transitions (Fig. 2). Figure 2a exhibits the emission spectra of complex **5** in 2-MeTHF solution and as neat film, and ECL and EL spectra, respectively. The emission maximum
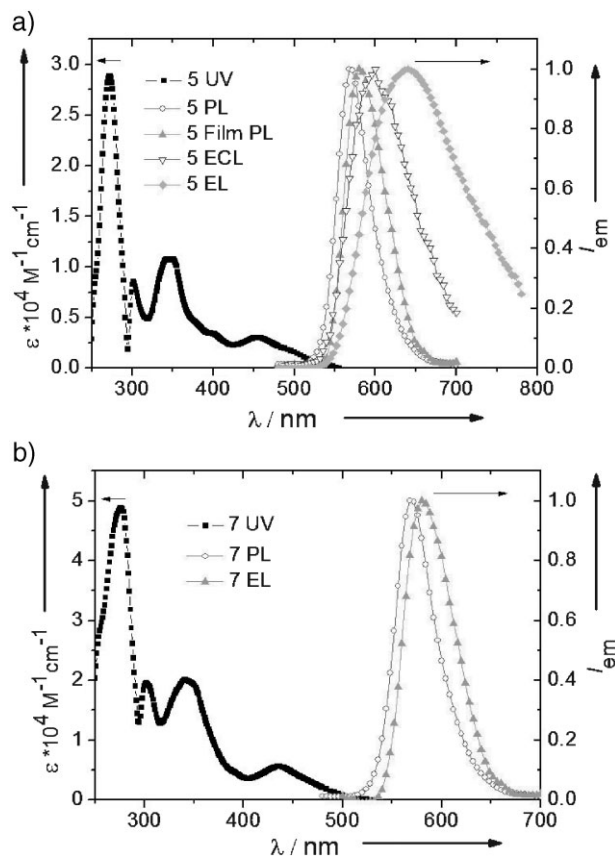

Figure 2. Photophysical spectra of complexes **5** (a) and **7** (b). The UV and PL spectra were obtained in 0.02 mM 2-MeTHF at 298 K. ECL spectrum of **5** was measured in 0.025 mM CH_3CN at 298 K. Film PL of **5** was obtained by dissolving **5** (20 mg) in 1 mL of 2-ethoxyethanol and PEO (20 mg) in 0.5 mL of $CHCl_3$, and then spin coating of the resulting mixed solution. EL spectra were measured at 5 V.

($\lambda_{max} = 580$ nm) of the PL spectrum of the neat film of complex **5** is a little red shifted compared to that of the solution spectrum ($\lambda_{max} = 570$ nm, $\phi_{PL} = 0.14$). This is thought to be due to self-aggregation. ECL in complex **5** was also observed under applying a pulsed voltage corresponding to the oxidation and reduction of the complex: The solution consisted of 0.025 mM complex **5** and 0.1 M $TBAPF_6$ as the supporting electrolyte in acetonitrile. The recombination between the redox precursors produced excited states of the complexes, and the consequent emission was detected by an N_2-cooled CCD camera. The ECL spectrum ($\lambda_{max} = 600$ nm) was slightly red shifted due to the different solvent polarities. This means that the same ^{3}MLCTs probably occur during the annihilation process. However, compared with the solution PL, the EL emission maximum ($\lambda_{max} = 640$ nm) of complex **5** is dramatically red shifted by about 70 nm. Figure 2b also shows the red shift of the EL emission maximum of complex **7** ($\lambda_{max} = 600$ nm) compared to that of the PL spectrum ($\lambda_{max} = 550$ nm, $\phi_{PL} = 0.31$). These interesting spectral shift effects for LECs have been reported several times previously.[7a,10,11,15] Although the reason for the shift is unclear, we assume that it is due to the polarization effect of the molecular orbitals under the high electric field in the device, as suggested by Wang et al.[11]

Table 1. Photophysical and device properties of Ir complexes

	$\lambda_{max,PL}$ [a] [nm]	ϕ_{PL} [b]	$\lambda_{max,EL}$ [c] [nm]	L_{lum}, [d] [cd/m^2]	$V_{turn-on}$	t_{min} [e]
5	570	0.14	640	990	3.6	0.5
7	550	0.31	600	1213	5.4	30

[a] Measured in 0.02 mM 2-MeTHF solution. [b] Quantum efficiency measurements were carried out at 298 K in 2-MeTHF solution. Solution of (pq)$_2$Iracac ($\phi_{PL} = 0.10$ in 2-MeTHF) was used as a reference [14]. [c] EL spectra of the LEC device were measured at -5 V. [d] Maximum brightness at -6.8 and -7.6 V for **5** and **7**, respectively. [e] Time required to reach 1 cd/m^2 at constant voltage -3 V.

Table 2. Electrochemical data of Ir complexes [a].

Compl	Oxidative process			Reductive process		
	E_{ox}°, V	i_{pc}/i_{pa}	ΔE_{pp}, V	E_{red}°, V	i_{pa}/i_{pc}	ΔE_{pp}, V
5	0.92	0.42	0.083	−1.75	0.32	0.074
7	1.29	0.54	0.126	−1.45	0.95	0.070

[a]. All of the electrochemical data were determined at room temperature in CH_3CN solution containing 0.1 M $TBAPF_6$.

2.2.2. Electrochemical Studies

The electrochemical properties of the compounds were studied using cyclic voltammetry (scan rate: $0.2\,V\,s^{-1}$) in CH_3CN solutions (1.0 mM) with 0.1 M $TBAPF_6$ as the supporting electrolyte. A glassy carbon electrode was employed as the working electrode and referenced with respect to a Ag quasi-reference electrode. All potential values were calibrated against a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. Although complexes **5** and **7** have the same main ligand, their oxidation and reduction potentials were different. The oxidation and reduction potentials for **5** were 0.92 and −1.75 V, while those for **7** were 1.29 and −1.45 V, respectively (Table 2). These differences are derived from the different π-acceptor abilities of the ancillary ligands. The iridium metal center of **7** has a more electron deficient environment than that of **5**. This is because the bpy of **7** with two nitrogens act as a better π-acceptor than the picolinic acid (pic) unit of **5** with one nitrogen. As a result, the oxidation potential of **7** is higher than that of **5**. Also, the reduction potential of **7** is lower than that of **5**. This is because the energies of the π^* orbital decrease in the order of pic > pq > bpy, based on a previously reported DFT calculation and experimental results.[9a,b,18] This means that the LUMO of complex **5** resides in the pq ligand, while that of complex **7** is in the bpy ligand. However, the electrochemical band gaps ($\Delta E^\phi = E_{ox} - E_{red}$) for **5** and **7** are similar (2.67 eV and 2.75 eV) to each other. The oxidative process shows that the peak current ratio (i_{pc}/i_{pa}) and peak separation (ΔE_{pp}) for **5** were 0.42 and 83 mV, while those for **7** were 0.54 and 126 mV, respectively. Both complexes **5** and **7** display a quasi-reversible one-electron-process both in oxidation and reduction
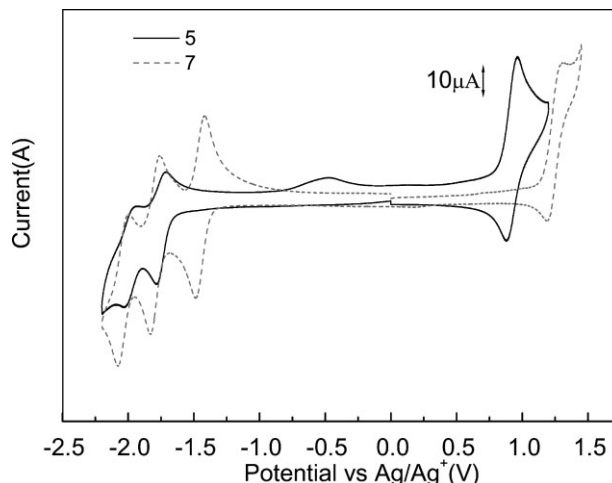
Figure 3. Cyclic voltammograms of 1 mM complex **5** (solid line) and **7** (dashed line). The scan rate was $0.2\,V\,s^{-1}$, and the supporting electrolyte was 0.1 M $TBAPF_6$.

concerning the peak current ratio (i.e., i_{pc}/i_{pa} in oxidation and i_{pa}/i_{pc} in reduction) and the peak-to-peak separation (ΔE_{pp}) (Fig. 3). As the excited states are generated by the electrochemical recombination of the redox couple, quasi-reversible electrochemistry of a complex is significant condition for an efficient LEC device.

2.3. Device Studies

LEC devices with **5** and **7** were prepared using the following configurations: ITO/**5** (20 mg) + PEO (20 mg) (100–110 nm)/Au and ITO/**7** (30 mg) + PEO (10 mg) (100–110 nm)/Au. Due to the phase separation resulting from the different polarities of the materials, different conditions were used for the active layer. As shown in the AFM image (Fig. 4a), neat films (**5** or **7** + PEO) with 100–110 nm thickness were obtained with a root-mean-square (RMS) roughness of ca. 4 nm. The polar sulfonate group enhanced the solubility in the polar solvent (2-ethoxyethanol)
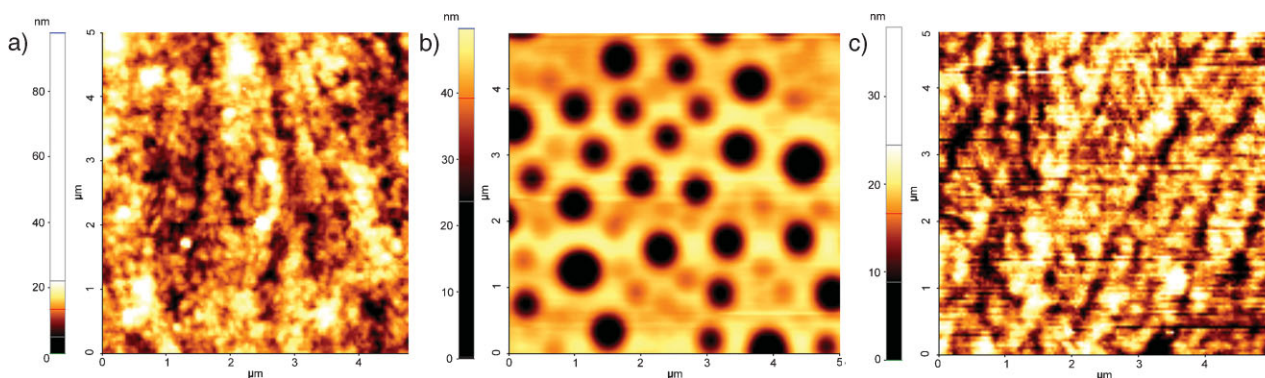
Figure 4. AFM images of neat films fabricated from a) complex **5** in 2-ethoxyethanol, b) complex **7** in DCM, and c) complex **7** in DCM:DCB (1:1). (a) and (b) were obtained by mixing with PEO in $CHCl_3$.

and miscibility with PEO. This resulted in complex **5** having a good morphology. Films of complex **7** in dichloromethane (DCM) show a rougher morphology (RMS roughness of ca. 8 nm) but pinholes were observed in the films (Fig. 4b), where no emission was observed. To minimize the extent of holes in the sample, dichlorobenzene (DCB) was used as a cosolvent. As a result, uniform spin-coated thin films (RMS ca. 4 nm) with no holes and no particular aggregation features or no phase separation could be obtained as shown in Figure 4c, which can emit the light under the bias (see the Experimental Section for the device condition).

In LEC devices, the size of the counterions is known to be one of most crucial factors in controlling the production rate of the electric field at the electrodes. We expect that small cations, such as Na$^+$, produce the electric field faster than larger counter anions. Therefore, small cations can reduce the turn-on time. Figure 5 compares the light output versus voltage for the fabricated devices. As the voltage increases, complex **5** emits red light at -3.6 V, which is a little higher than its electrical gap ($\Delta E^\phi = 2.67$ eV). This discrepancy is due to the time required for the Na$^+$ to reach the electrode under reverse bias. However, above the turn-on voltage, complex **5** continuously emitted light like OLEDs as the voltage increases. In contrast, complex **7** needed a higher turn-on voltage (5.4 V) than complex **5**, although the electrochemical gap ($\Delta E^\phi = 2.75$ eV) for complex **7** is similar. This result indicates that the counter anion (PF$_6^-$) requires a longer time to reach the electrode compared to Na$^+$. The maximum luminance reached was 990 cd m^{-2}, with a current efficiency of 0.23 cd A^{-1} at -6.8 V for **5**, and 1210 cd m^{-2} with a current efficiency of 0.23 cd A^{-1} at -7.6 V for complex **7**. Under forward bias, the turn-on voltage was 4.8 V for complex **5** and 5.4 V for complex **7**. The reason for the different turn-on voltages (-3.6 and 4.8 V) for complex **5** is not clear, but we assume that this may be due to some kind of repulsion between the Au and Na$^+$. Therefore, Na$^+$ ions will take a longer time to reach the Au electrode under forward bias.

A distinct characteristic of LECs is that they can be operated at a bias voltage close to their electrochemical gap.[8] Thus, the devices based on complexes **5** and **7** were tested under a bias of -3 V,
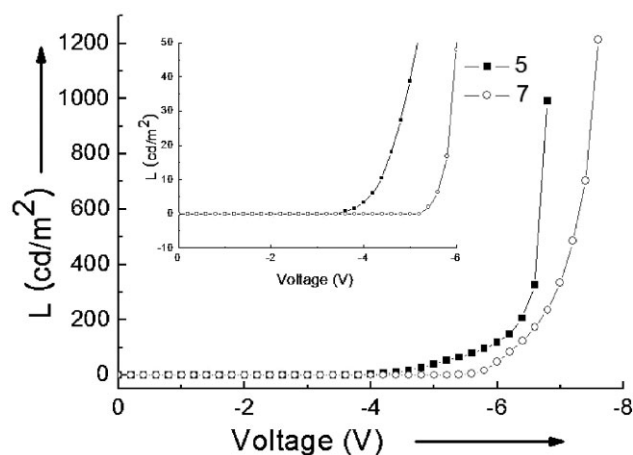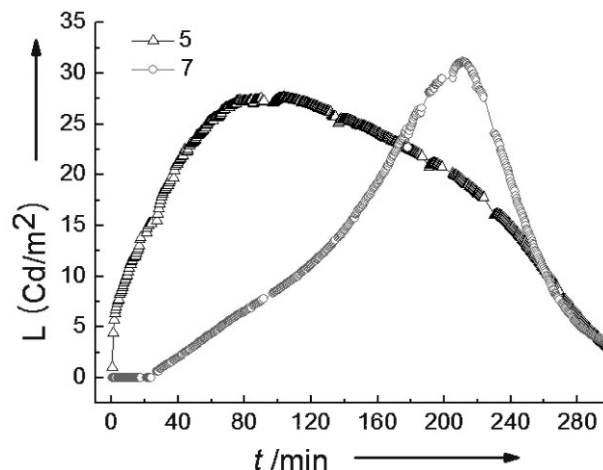
Figure 6. The time-dependent luminance of single-layered LEC device of complex **5** and **7** at -3 V.

which is similar to their electrochemical gaps. Time-dependent brightness is shown in Figure 6. The turn-on times required to reach 1 cd m^{-2} were quite different for the two complexes at constant -3 V. Complex **5** took less than 0.5 min to emit a red color, while complex **7** took 30 min to do the same. Due to a faster counter ion distribution time, complex **5** exhibited a faster response time than did complex **7**. To the best of our knowledge, the reported fastest response time based on iridium complexes for LECs, is 2.5 min.[9e] Compared to this result, complex **5** obviously showed improved response time over 5-fold. With increasing current, the brightness reached a maximum of 27 cd m^{-2} for complex **5** after 75 min. On the other hand, complex **7** took 210 min to reach its maximum luminance of 30 cd m^{-2}. In addition, the neutral Ir complex **5** showed better device stability than the ionic Ir complex **7** (Fig. 6). Previous reports have shown that with a decreasing counter anion size, the turn-on time improves, but the device stability decreases.[3c,d,7b] By contrast, we not only obtained a shorter response time, but also better stability. The lifetimes of the devices (lifetime is defined as the time taken for the brightness of the device to decay to half its maximum under constant bias) were 3 h for complex **5** and 0.5 h for complex **7**.

3. Conclusions

In conclusion, we have reported an example of a neutral iridium complex (**5**) containing a pendant Na$^+$ ion in a LEC. The LEC derived from **5** exhibited a 60-fold faster turn-on time compared to the iTMC (**7**) with PF$_6^-$. This result is presumably due to the faster delivery of the Na$^+$ ions to the electrode compared to the PF$_6^-$ ions. Also, the device lifetime of complex **5** exhibited a six-fold increase in stability and a three-fold shorter time to reach maximum brightness at constant bias compared to the device made with complex **7**. This new system still has problems, such as low efficiency, low stability, and low brightness when compared to OLEDs. However, our study suggests that the new strategy using

Figure 5. Plot of luminance versus voltage under reverse bias. Device configurations for **5** and **7** were ITO/**5** (20 mg) + PEO (20 mg) (100–110 nm)/Au and ITO/**7** (30 mg) + PEO (10 mg) (100–110 nm)/Au, respectively. The inset shows a magnification of the turn-on region.

cation transport in a single layer is able to improve the turn-on time and stability compared to those of iTMC-based LECs. In future, different cation sizes will be tested to help develop LECs with even better performance.

4. Experimental

Device Fabrication: Device 5: 20 mg of **5** in 1 mL of ethoxyethanol was mixed with 20 mg of PEO in 0.5 mL $CHCl_3$. A thin film was spin-cast into ITO electrode at stepwise speeding, 500 rpm for 5 s, 1500 rpm for 30 s, and 700 rpm for 10 sec. And then on to this film Au was deposited with 100 nm thickness.

Device 7: 30 mg of **7** dissolved in CH_2Cl_2 (0.5 mL) and dichlorobenzene (0.5 mL) was mixed with 10 mg of PEO in 0.5 ml $CHCl_3$. The other procedure is same to that of **5**.

Synthesis: Complex 4: A mixture of compound **3** (350 mg, 0.47 mmol), Cs_2CO_3 (308 mg, 0.95 mmol) and 1,4-butanesultone (451 mg, 3.31 mmol) in DMF was stirred at room temperature for 24 h. The solvent was evaporated in vacuum and dissolved in methylene chloride. The organic phase was washed with water, brine and dried over Na_2SO_4. The solvent was evaporated to give the crude product, which was applied to column chromatography on silica gel, eluting with methylene chloride and methyl alcohol (10:1, v/v) to provide the desired product (80 mg, 19% yield). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.76 (d, $J = 9$ Hz, 1H), 8.55 (d, $J = 9$ Hz, 1H), 8.45 (q, $J = 18$ Hz, 3H), 8.19 (d, $J = 9$ Hz, 1H), 8.02 (t, $J = 15$ Hz, 2H), 7.95 (d, $J = 9$ Hz, 1H), 7.52 (m, $J = 39$ Hz, 6H), 7.28 (d, $J = 9$ Hz, 1H), 7.06 (q, $J = 12$ Hz, 2H), 6.94 (t, $J = 9$Hz, 1H), 7.68 (t, $J = 9$ Hz, 1H), 6.59 (q, $J = 6$ Hz, 2H), 6.05 (d, $J = 6$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 170.27, 169.46, 169.08, 157.43, 151.71, 150.65, 147.98, 147.04, 146.90, 145.98, 140.14, 139.47, 139.30, 137.69, 134.99, 133.92, 131.04, 130.05, 129.65, 129.15, 128.84, 128.39, 127.67, 127.33, 127.18, 126.53, 126.30, 126.25, 126.05, 124.55, 124.27, 121.51, 120.93, 117.45, 117.40, 68.87, 60.61, 51.40, 50.87, 27.47, 21.77, 21.62. HRMS: calcd for $C_{40}H_{32}IrN_3O_6S$, 875.1641; found, 875.1728.

Complex 5: A mixture of compound **4** (100 mg, 0.11 mmol) and NaOH (5 mg, 0.13 mmol) in methyl alcohol was stirred at room temperature for 24 h. The solvent was evaporated to give the orange-red solid, which was recrystallized in dichloromethane and hexane (90 mg, 88% yield). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.76 (d, $J = 9$ Hz, 1H), 8.55 (d, $J = 9$ Hz, 1H), 8.45 (q, $J = 18$ Hz, 3H), 8.19 (d, $J = 9$ Hz, 1H), 8.02 (t, $J = 15$ Hz, 2H), 7.95 (d, $J = 9$ Hz, 1H), 7.52 (m, $J = 39$ Hz, 6H), 7.28 (d, $J = 9$ Hz, 1H), 7.06 (q, $J = 12$ Hz, 2H), 6.94 (t, $J = 9$ Hz, 1H), 7.68 (t, $J = 9$ Hz, 1H), 6.59 (q, $J = 6$ Hz, 2H), 6.05 (d, $J = 6$ Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 170.27, 169.46, 169.08, 157.43, 151.71, 150.65, 147.98, 147.04, 146.90, 145.98, 140.14, 139.47, 139.30, 137.69, 134.99, 133.92, 131.04, 130.05, 129.65, 129.15, 128.84, 128.39, 127.67, 127.33, 127.18, 126.53, 126.30, 126.25, 126.05, 124.55, 124.27, 121.51, 120.93, 117.45, 117.40, 68.87, 60.61, 51.40, 50.87, 27.47, 21.77, 21.62. HRMS: calcd for $C_{40}H_{32}IrN_3$. NaO_6S, 898.1539; found, 898.1537.

Complex 7: A mixture of compound **2** (350 mg, 0.26 mmol) and 2,2′-bipyridine (64 mg, 0.41 mmol) was refluxed in an inert atmosphere in 2-ethoxyethanol for 8–10 h. After cooling to room temperature, the solvent was evaporated in high vacuum and the residue was dissolved in methanol. To a solution of the residue in methanol was added NH_4PF_6 (64 mg, 0.41 mmol). After stirring overnight at room temperature, the resulting mixture was subsequently filtered through a Büchner funnel and then washed with hexane and ethyl ether several times to provide orange solid (200 mg, 27.7% yield). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.56 (q, $J = 39$ Hz, 2H), 8.37 (d, $J = 39$ Hz, 1H), 8.23 (d, $J = 33$ Hz, 1H), 8.10 (q, $J = 30$ Hz, 2H), 7.93 (d, $J = 6$ Hz, 1H), 7.68 (t, $J = 12$ Hz, 1H), 7.42 (t, $J = 15$ Hz, 1H), 7.18 (q, $J = 24$ Hz, 2H), 7.07 (t, $J = 15$ Hz, 1H), 6.82 (t, $J = 15$ Hz, 1H), 6.41 (d, $J = 9$ Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 169.69, 154.98, 150.86, 147.29, 146.71, 145.74, 140.39, 139.78, 133.73, 130.93, 130.59, 129.36, 128.35, 127.67, 127.41, 126.74, 124.20, 123.99, 122.69, 118.18. HRMS: calcd for $C_{40}H_{28}F_6IrN_4P$, 902.1585; found, 902.1602.

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