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Decreased Turn-On Times of Single-Component Light-Emitting Electrochemical Cells by Tethering an Ionic Iridium Complex with Imidazolium Moieties

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Abstract: We report a significant decrease in turn-on times of light-emitting electrochemical cells (LECs) by tethering imidazolium moieties onto a cationic Ir complex. The introduction of two imidazolium groups at the ends of the two alkyl side chains of $[Ir(ppy)_2(dC6\text{-}daf)]^+(PF_6)^-$ (ppy = 2-phenylpyridine, dC6-daf = 9,9′-dihexyl-4,5-diazafluorene) gave the complex $[Ir(ppy)_2(dC6MIM\text{-}daf)]^{3+}[(PF_6)^-]_3$ (dC6MIM-daf = 9,9-bis[6-(3-methylimidazolium)hexyl]-1-yl-4,5-diazafluorene). Both complexes exhibited similar photoluminescent/electrochemical properties and comparable electroluminescent efficiencies. The turn-on times of the LECs based on the latter complex, however, were much lower than those of devices based on the former. The improvement is ascribed to increased concentrations of mobile counterions ($(PF_6)^-$) in the neat films and a consequent increase in neat-film ionic conductivity. These results demonstrate that the technique is useful for molecular modifications of ionic transition-metal complexes (ITMCs) to improve the turn-on times of LECs and to realize single-component ITMC LECs compatible with simple driving schemes.

Keywords: electrochemical cells · electroluminescence · ionic liquids · iridium · light-emitting devices

Introduction

Solid-state light-emitting electrochemical cells (LECs) have several advantages over conventional organic light-emitting diodes (OLEDs). In LECs, electrochemically doped regions induced by spatially separated ions under a bias form ohmic contacts with electrodes to give balanced carrier injection, low operating voltages, and consequently high power efficiencies.[1–3] As such, LECs generally require only a single emissive layer, which can be easily processed from solutions, and can conveniently use air-stable electrodes, whereas OLEDs typically require more-sophisticated multilayer structures and low-work-function cathodes.[4,5] Compared with conventional polymer LECs that are usually composed of an emissive conjugated polymer, a salt, and an ion-conducting polymer,[1–3] LECs based on ionic transition-metal complexes (ITMCs) show several further advantages and have attracted much attention in recent years.[6–30] In such devices, no ion-conducting material is needed as these metal complexes are intrinsically ionic. Furthermore, higher electroluminescence (EL) efficiencies are expected owing to the phosphorescent nature of the metal complexes. Recently, we reported highly efficient green and orange LECs (external quantum efficiency (EQE) > 7 % photon/electron) made from neat films of ionic iridium complexes with a bulky diazaspirobifluorene-based auxiliary ligand for superior steric hindrance and to retain high efficiency in the neat films.[28] An even higher EQE, > 10 % (power efficiency > 36 lm W^{-1}), was achieved with a host–guest LEC configuration,[3,25] which was prepared by doping the orange-emitting Ir complex (guest) into the green-emitting one (host) and effectively suppressing the self-quenching effects.[29]

Although ITMC LECs have several promising advantages, they usually suffer from long turn-on times (t_{max}, the time taken to reach maximum brightness after a constant bias is applied) ranging from seconds to several hours due to the time needed for counterions to drift and accumulate near electrodes under an electric field.[6–30] To achieve practical

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application, several techniques for improving the turn-on times of ITMC LECs, such as decreasing the thickness of the emissive layer,[18] increasing the applied bias,[8,13] prebiasing,[8] and increasing the ionic conductivity of the emissive layer,[7,14,23,27] have been reported. Decreasing the thickness of the emissive layer of ITMC LECs diminishes the turn-on time, but deteriorates the device efficiency due to exciton quenching near electrodes.[18] Increasing the bias voltage of ITMC LECs shortens the turn-on time, but leads to a lower peak EQE value and a higher degradation rate.[8,13] The use of a prebiasing technique, in which a higher bias than necessary is first applied for a brief period, helps to accelerate the turn-on time of the LEC device.[8] However, the prebiasing technique complicates the driving circuits and the integration process for applications. Addition of $LiCF_3SO_3$/poly-(ethylene oxide),[7] $LiCF_3SO_3$/crown ether,[14] and ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIM^+(PF_6)^-$)[23] into the emissive layer of ITMC LECs increases the concentration of mobile ions. This in turn increases the ionic conductivity of the emissive layer as the current in the device under the same electric field increases. Therefore, the time needed for enough ions to accumulate near the electrodes under an applied field to turn on the device is decreased. However, the mixing of two- or three-component systems complicate the fabrication process and could also cause issues of phase compatibility between components, non-uniformity,[7] and device stability.[23]

The chemical attachment of ionically charged ligands to metal complexes represents an alternative and promising approach to increase the ionic conductivity and to improve the turn-on speed of LECs, as phase compatibility is less of an issue in such configurations. Bolink et al. reported a homoleptic iridium complex containing ionically charged ligands, which give a net charge of +3 for each complex.[27] The LEC based on this complex showed a much improved turn-on time, but also suffered from other issues, for example, color shift during operation and low efficiency, that are relevant to practical applications as well. Recently, Zysman-Colman et al. also reported homoleptic ruthenium-based and heteroleptic iridium-based ITMCs containing tethered ionic tetraalkylammonium salts.[31] Similarly, LECs constructed by using such complexes also exhibited decreased turn-on times; however, the EL efficiencies of these complexes were not satisfactory in comparison to general EL efficiencies achievable with ITMCs. Hence, further studies on ITMCs containing ionically charged ligands that can give improved turn-on times, stable operation, and high emission efficiency are still highly needed.

In this paper, we demonstrate the decrease in turn-on times of single-component iridium-based ITMC LECs with tethered imidazolium moieties. This new ITMC is achieved by fusing two imidazolium groups at the ends of the two alkyl side chains of a more conventional ITMC, [Ir(ppy)$_2$(dC6-daf)]$^+$(PF$_6$)$^-$ (**1**; ppy = 2-phenylpyridine, dC6-daf = 9,9′-dihexyl-4,5-diazafluorene), to form the new complex [Ir(ppy)$_2$(dC6MIM-daf)]$^{3+}$[(PF$_6$)$^-$]$_3$ (**2**; dC6MIM-daf = 9,9-bis[6-(3-methylimidazolium)hexyl]-1-yl-4,5-diazafluorene)

(Scheme 1). To study the effects of the chemical tethering of imidazolium groups on the properties of ionic iridium complexes, the photophysical, electrochemical, and LEC characteristics of complex **2** are compared with those of the reference complex **1**. Experimental results show that although both complexes exhibit similar photoluminescence (PL)/electrochemical properties and comparable EL efficiencies, the turn-on times of the LECs based on **2** are significantly shorter than those of devices based on **1**. This indicates that chemical attachment of ionic iridium complexes with imidazolium groups increases the ionic conductivity of the films but does not influence their emissive properties as much. Such techniques should be useful in the molecular modification of ITMCs to obtain desired characteristics.

Results and Discussion

Synthesis

The synthesis of complexes **1** and **2** is shown in Scheme 1. The ligands dC6-daf (**3**) and dC6Br-daf (**4**) were synthesized by nucleophilic substitution of the 4,5-diazafluorene anion generated by NaH deprotonation with 1-bromohexane and 1,6-dibromohexane, respectively. The dibromo intermediate
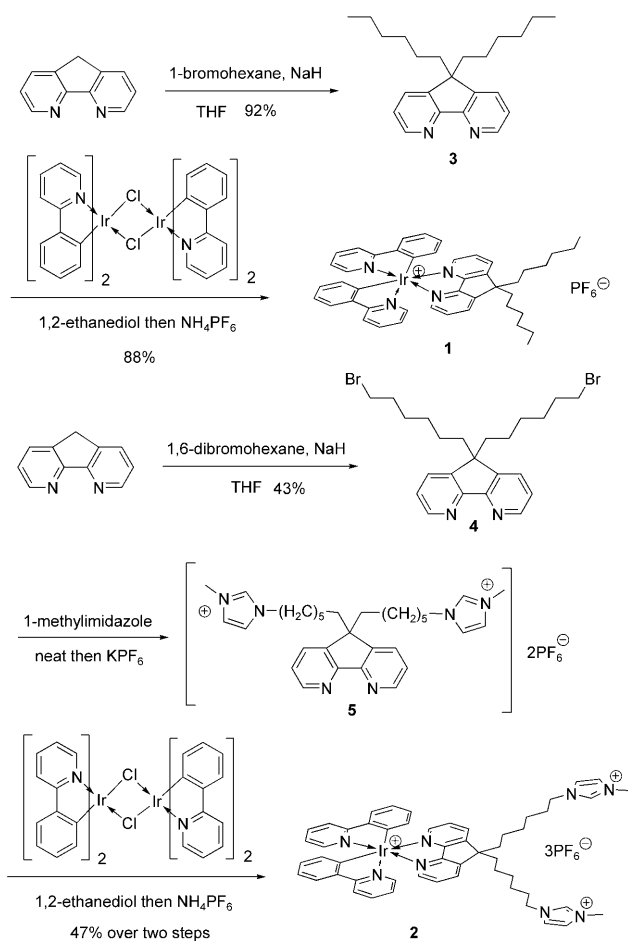
Scheme 1. Synthetic pathways and structures of complexes **1** and **2**.

4, which suffered from self-polymerization, could only be obtained in 43% yield. Instead of using pure dC6MIM-daf (**5**) for the subsequent complexation, we prepared it in situ by treating dibromo compound **4** with neat 1-methylimidazole directly, followed by ion-exchange with potassium hexafluorophosphate to afford **5**, which was subjected to complexation with the chloro-bridged dimeric iridium complex by adapting a literature procedure[33–35] to give the complexes **1** and **2**.

Photophysical Properties

Homogeneous thin films of both complexes **1** and **2** were obtained by spin-casting from solution in CH_3CN. We also tried to prepare a physically blended film of **1** and ionic liquid $BMIM^+(PF_6)^-$ for comparative studies; however, the resulting cloudy films indicated strong phase separation and incompatibility between **1**, which has long alkyl chains, and the ionic liquid, which is highly polar. Figure 1a and b
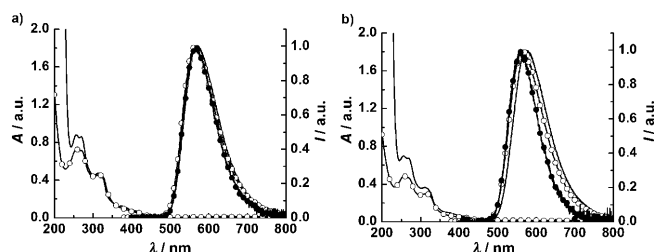

Figure 1. Absorption and PL spectra in CH_2Cl_2 (10^{-5} M) (——) and as neat films (○), as well as EL spectra (●), with a forward bias voltage of 2.8 V for complexes a) **1** and b) **2**.

shows the UV/Vis and PL spectra of **1** and **2**, respectively, in CH_2Cl_2 (10^{-5} M) and as neat films (≈ 100 nm). Similar absorption features were observed for both complexes either in solution or as films. The absorption spectra of these compounds show intense bands ($\varepsilon > 10^4$ M^{-1} cm^{-1}) in the UV part of the spectrum (200–350 nm), which are associated with the ligand-centered (LC) transitions of the ligands.[24,26] These LC bands are accompanied by weaker, broad bands ($\varepsilon \approx (1–5) \times 10^3$ M^{-1} cm^{-1}) extending from 350 to just over 400 nm, which are associated with the metal-to-ligand charge-transfer (MLCT) transitions (both allowed and spin-forbidden).[24,26] The high intensity of the MLCT bands in Ir-based complexes was attributed to the effective mixing of these charge-transfer transitions with the energetically higher-lying spin-allowed transitions of the ligands.[24,26] The mixing is facilitated by the strong spin–orbit coupling of the Ir^{III} center. Solution PL emission is in the yellow range (≈ 570 nm) for both complexes **1** and **2**, which indicates that tethering of imidazolium groups at the

ends of the alkyl chains in **1** has no significant modulating effect on the energy gaps.

The PL quantum yields (QYs) of complexes **1** and **2** in CH_2Cl_2, determined with a calibrated integrating sphere (see Experimental Section for details), are 0.59 and 0.47, respectively (Table 1). Room-temperature transient PL data of **1** and **2** in CH_2Cl_2, determined by the time-correlated single-photon-counting technique (see Experimental Section for details), exhibit single-exponential-decay behavior, and the extracted excited-state lifetimes for **1** and **2** are 1.12 and 0.94 μs, respectively (Table 1). Excited-state lifetimes on the order of microseconds are the signature of phosphorescence, which is associated with emission from the ^{3}MLCT states of the complexes formed through strong intersystem crossing mediated by the iridium atom. Spin-coated neat films of complexes **1** and **2** exhibit PL spectra similar to those observed for their solutions (Figure 1). The measured PL QYs and excited-state lifetimes of the neat films are, respectively, 0.33 and 0.66 μs for **1** and 0.35 and 0.75 μs for **2** (Table 1). The lower PL QYs and shorter excited-state lifetimes for the neat films indicate that interaction between closely packed molecules provides additional deactivation pathways. However, the PL QYs of **1** and **2** as neat films still retain about 56 and 75% of the values in solution. The highly retained PL QYs for the neat films of **1** and **2** are likely to be associated with their sterically bulky dC6-daf and dC6MIM-daf ligands. Notably, self-quenching in neat films of complex **2** is not as severe as that in neat films of complex **1** perhaps due to better steric hindrance provided by the imidazolium groups in **2**.

Cyclic Voltammetry

Figure 2 depicts the electrochemical characteristics of complexes **1** and **2** probed by cyclic voltammetry (CV; see Experimental Section for experimental details), and the measured redox potentials are summarized in Table 1. Complexes **1** and **2** exhibit reversible redox peaks at similar potentials (vs. Ag/AgCl); there is a reversible oxidation potential at 1.33 and 1.31 V for **1** and **2**, respectively, and a reversible reduction potential at -1.47 and -1.48 V for **1** and **2**, respectively. The highest occupied molecular orbital (HOMO) of $[Ir(ppy)_2(N^{\wedge}N)]PF_6$ complexes was reported to be a mixture of the orbitals of iridium and the phenyl group of the $C^{\wedge}N$ ligand, whereas the lowest unoccupied molecular orbital (LUMO) is mostly localized on the $N^{\wedge}N$

Table 1. Physical properties of complexes **1** and **2**.

Complex	$\lambda_{max,PL}$ [nm][b]		PL QY		τ [μs][c]		$E_{1/2}^{ox}$ [V][d]	$E_{1/2}^{red}$ [V][e]	$\Delta E_{1/2}$ [V][f]
	Solution[a]	Neat film	Solution[a]	Neat film	Solution[a]	Neat film			
1	568	562	0.59	0.33	1.12	0.66	+1.33	−1.47	2.80
2	570	562	0.47	0.35	0.94	0.75	+1.31	−1.48	2.82

[a] Measured in CH_2Cl_2 (10^{-5} M) at room temperature. [b] PL peak wavelength. [c] Excited-state lifetimes. [e] Oxidation potential. [f] Reduction potential. [g] The electrochemical gap $\Delta E_{1/2}$ is the difference between $E_{1/2}^{ox}$ and $E_{1/2}^{red}$.
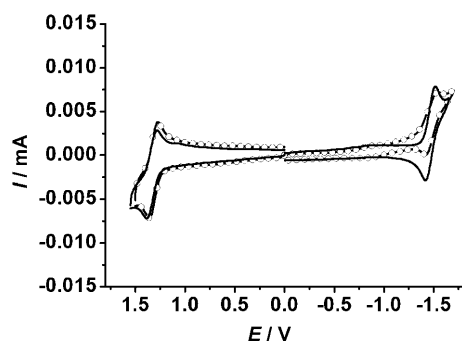
Figure 2. Cyclic voltammogram of complexes **1** (——) and **2** (○). All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode.

ligand.[28] As the structures of **1** and **2** differ only in the terminal alkyl chain of the N^N ligand, their HOMO and LUMO distributions should be similar and should give similar redox potentials. The presence of imidazolium moieties in **2** exhibited limited influence on the electrochemical properties of the Ir center, especially for the frontier molecular orbitals.

Clearly, the peak current of complex **2** is lower than that of complex **1** at around -1.40 V. Similar behavior was also observed upon mixing complex **1** with the ionic liquid $BMIM^+(PF_6)^-$ (2 equiv). Increasing the CV scan rate from 100 to 400 mV s^{-1} gave a higher peak current. These results indicate that the pendant imidazolium ions may interact with the reduced species and consequently retard the diffusion toward the electrode.

Device Results

In the operation of LEC devices, when a constant bias voltage is applied, a delayed EL response, associated with the time needed for counterions to be redistributed in the LECs, is typically observed. In the case of neat films of ionic iridium complexes, the redistribution of the anions (($PF_6)^-$) leads to formation of a region of Ir^{IV}/Ir^{III} complexes (p type) near the anode and a region of Ir^{III}/Ir^{II} complexes (n type) near the cathode.[15] With the formation of p and n regions near the electrodes, carrier injection is enhanced, thus leading to gradually increasing device current and emission intensity. Device characteristics based on the structure of the glass substrate/indium tin oxide (ITO)/**1** or **2** (100 nm)/Ag device are discussed below and summarized in Table 2. The EL spectra of the devices based on complexes **1** and **2** are shown in Figure 1a and b, respectively, for comparison with their PL spectra. The EL spectra are basically similar to the PL spectra, which indicates similar emission mechanisms. Time-dependent brightness and current densities of the LEC device based on complex **1** operating at 2.7 and 2.8 V are shown in Figure 3a. The current in the device increased slowly with time after the bias was applied and kept increasing even after 10 h of operation. The time for turning on the device ($t_{\text{turn-on}}$), defined as the time to achieve a brightness of 1 cd cm^{-2}, was 65 min at 2.8 V. The brightness increased

Table 2. Characteristics of LEC devices based on complexes **1** and **2**.

Complex (bias [V])	$\lambda_{\text{max,EL}}$ [nm][a]	$t_{\text{turn-on}}$ [min][b]	t_{max} [min][c]	L_{max} [cd cm^{-2}][d]	$\eta_{\text{ext,max}}$ [%], $\eta_{\text{p,max}}$ [lm W^{-1}][f]
1 (2.8)	566	65	500	105	5.5, 18.7
1 (2.7)	566	84	>600	>56[e]	5.5, 19.2
2 (2.8)	577	12	200	79	4.0, 14.7
2 (2.7)	577	16	200	31	4.5, 17.1

[a] EL peak wavelength. [b] Time required to reach a brightness of 1 cd cm^{-2}. [c] Time required to reach the maximum brightness. [d] Maximum brightness achieved at a constant bias voltage. [e] Maximum brightness was not reached after 10 h. [f] Maximum external quantum efficiency and maximum power efficiency achieved at a constant bias voltage.
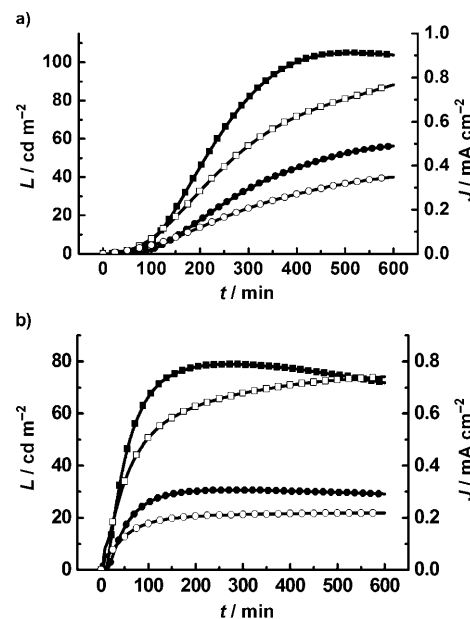

Figure 3. Dependence of brightness (filled symbols) and current density (empty symbols) on time at 2.7 (circles) and 2.8 V (squares) for the single-layered LEC devices based on complexes a) **1** and b) **2**.

with current and reached a maximum of 105 cd m^{-2} in about 500 min at 2.8 V. For devices at 2.7 V, the brightness reached 56 cd m^{-2} and was still increasing at 600 min. Comparatively, the LEC based on complex **2** showed a much faster response. As shown in Figure 3b, this device turned on sharply in 12 min at 2.8 V and took only about 200 min to reach the maximum brightness of 79 and 31 cd m^{-2} at 2.8 and 2.7 V, respectively. Such improved turn-on times confirm that chemically tethering imidazolium groups onto complex **2** increases the density of mobile counterions (($PF_6)^-$) in the neat films and consequently increases the neat-film ionic conductivity.

Efficient LECs are essential for operation at a practical brightness with the lowest possible bias, which would ensure the stable operation of LECs.[8,13,16,19,28] Hence, it is important to examine the effect of chemical tethering of imidazolium groups with an ionic iridium complex on the device efficiencies of LECs. Time-dependent EQE values and the corresponding power efficiencies of the device based on complex **1** with biases of 2.7 and 2.8 V are shown in Fig-

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ure 4a. When a forward bias had just been applied, the EQE was rather low due to unbalanced carrier injection. During the formation of the p- and n-type regions near the
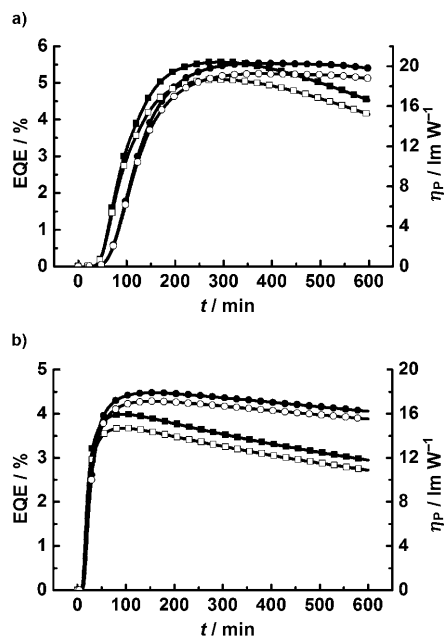

Figure 4. Dependence of EQE (filled symbols) and corresponding power efficiency (empty symbols) on time at 2.7 (circles) and 2.8 V (squares) for the single-layered LEC devices based on complexes a) **1** and b) **2**.

electrodes, the balance of the carrier injection was improved, and the EQE of the device increased rapidly. The peak EQE value and the peak power efficiency for the device based on complex **1** with biases of 2.8 and 2.7 V are 5.5% and 18.7 lm W^{-1}, and 5.5% and 19.2 lm W^{-1}, respectively. The time-dependent evolution trend in device efficiency of the device based on complex **2** is similar to that of the device based on complex **1**, but it took much less time (within 100 min) for the former to reach the peak device efficiency. The peak EQE value and the peak power efficiency for the device based on complex **2** at 2.8 and 2.7 V are 4.0% and 14.7 lm W^{-1}, and 4.5% and 17.1 lm W^{-1}, respectively. The EL efficiencies of both devices are comparable, which indicates that chemical tethering of imidazolium groups with an ionic iridium complex gives a faster device response but does not influence the EL efficiencies significantly. Hence, the technique of integrating ionic-liquid moieties onto the ITMC directly serves as a useful and promising alternative to improve the turn-on speed of LECs and to realize single-component ITMC LECs that are compatible with simple driving schemes.

Conclusions

We have reported a significant decrease in turn-on times of single-component iridium LECs by the chemical tethering

of imidazolium moieties. The desired multifunctional complex was achieved by fusing two imidazolium groups at the two ends of the alkyl chain in $[Ir(ppy)_2(dC6\text{-}daf)]^+(PF_6)^-$ (**1**) to form the complex $[Ir(ppy)_2(dC6MIM\text{-}daf)]^{3+}[(PF_6)^-]_3$ (**2**). Experimental results show that both complexes exhibit similar PL/electrochemical properties and comparable EL efficiencies. The turn-on times of the LECs based on complex **2**, however, is much lowered compared to those of devices based on complex **1**. Improved turn-on times result from increased concentrations of mobile counterions $((PF_6)^-)$ in the neat films and a consequent increase in neat-film ionic conductivity. These results demonstrate that such a technique is useful for molecular modifications of ITMCs to improve turn-on times of LECs and to realize single-component ITMC LECs compatible with simple driving schemes.

Experimental Section

General

^{1}H and ^{13}C NMR spectra were collected on a 400 MHz spectrometer at room temperature. Photophysical data in solution were collected at room temperature by using a 10^{-5} M solution of **1** and **2** in CH$_2$Cl$_2$, which was purged with nitrogen gas for several minutes prior to measurement. Neat films of **1** and **2** were spin-coated onto quartz substrates from solutions in CH$_3$CN, and photophysical data were collected under ambient conditions. The thickness of the spin-coated films was about 100 nm, as measured by ellipsometry. UV/Vis spectra were recorded on a spectrophotometer. PL spectra were recorded by using a cooled charge-coupled device (CCD) coupled to a monochromator with the 325-nm line of a He/Cd laser as the excitation source. PL QYs for solution and thin-film samples were determined with a calibrated integrating sphere system. Excited-state lifetimes of samples were measured by using the time-correlated single photon counting (TCSPC) technique, in which a photomultiplier and a subnanosecond pulsed UV laser diode were used as the detector and the pulsed excitation source, respectively, and the PL signals were detected at the peak PL wavelengths. Oxidation and reduction potentials were determined by CV in solutions of **1** and **2** (1.0 mM) in CH$_2$Cl$_2$ containing 0.1 M of tetra-*n*-butylammonium hexafluorophosphate (TBAPF$_6$) as a supporting electrolyte at a scan rate of 100 mV s^{-1}. A glassy carbon electrode and a platinum wire were used as the working and counter electrodes, respectively. The redox couple of ferrocene/ferrocenium (Fc/Fc$^+$), which occurs at $E^{o'} = +0.47$ V in CH$_2$Cl$_2$/TBAPF$_6$, was used an internal standard for the oxidation and reduction of **1**; the redox potential of Fc/Fc$^+$ was observed to shift to $E^{o'} = +0.39$ V for the oxidation of **2**, and $E^{o'} = +0.42$ V for the reduction of **2** vs. Ag/AgCl (saturated). All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode.

ITO-coated glass substrates were cleaned and treated with UV/ozone prior to spin-coating of the emissive layer. The preparation of solutions of **1** and **2** and the spin-coating of neat films (≈ 100 nm) of **1** and **2** were performed under nitrogen atmosphere in a glove box. After spin-coating, the neat films were then baked at 70 °C for 15 h, followed by thermal evaporation of a 150-nm Ag top contact in a vacuum chamber ($\approx 10^{-6}$ Torr). The electrical characteristics of the LEC devices were measured by using a source-measurement unit and an Si photodiode calibrated with a Photo Research PR-650 spectroradiometer. All device measurements were performed at a constant bias voltage (2.7 or 2.8 V). EL spectra were recorded with a calibrated CCD spectrograph.

Syntheses

dC6-daf: 4,5-Diazafluorene[32] (500 mg, 2.97 mmol) and sodium hydride (357 mg of 60%, 8.92 mmol) were dissolved in THF (30 mL), and 1-bromohexane (1.26 mL, 8.92 mmol) was added in one portion. The mixture

was heated under reflux for 2 h, and the reaction was quenched with water. The solvent was evaporated, and the reaction mixture was extracted with diethyl ether and dried with $MgSO_4$. The crude product was purified by column chromatography on silica gel (hexane was used as eluent to remove excess 1-bromohexane, and the product was flushed out with ethyl acetate) to afford pure dC6-daf (920 mg, 92%) as a sticky, dark fluid. ^1H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 8.66$ (dd, $^3J_{H,H} = 4.8$ Hz, $^4J_{H,H} = 1.6$ Hz, 2H), 7.69 (dd, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.6$ Hz, 2H), 7.27 (dd, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 4.8$ Hz, 2H), 1.98 (t, $^3J_{H,H} = 4.0$ Hz, 4H), 1.14–0.99 (m, 12H), 0.76 (t, $^3J_{H,H} = 7.2$ Hz, 6H), 0.69–0.61 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): $\delta = 158.3$, 149.3, 144.7, 130.4, 122.7, 51.3, 39.3, 31.5, 29.6, 24.1, 22.5, 14.0 ppm; MS (ESI+): m/z (%) calcd for $C_{23}H_{33}N_2$: 337.2644 $[M+H]^+$; found: 337.2640 (100).

1: Bis-(μ)-chlorotetrakis(2-phenylpyridinato-C^2,N)diiridium(III)[33–35] (322 mg, 0.30 mmol) and 9,9-dihexyl-4,5-diazafluorene (212 mg, 0.63 mmol) were dissolved in 1,2-ethanediol (25 mL) under Ar, and the mixture was kept at 150°C for 16 h. The solution was cooled to room temperature, and an aqueous solution of NH_4PF_6 (750 mg in 7.5 mL deionized water) was added to yield a yellow suspension. The solid was then filtered and dried in an oven (80°C) for 12 h. The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$/MeCN = 10:1) to give **1** (544 mg, 88%) as a yellow solid. ^1H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 8.01$ (d, $^3J_{H,H} = 8.0$ Hz, 2H), 7.91 (d, $^3J_{H,H} = 8.0$ Hz, 2H), 7.76 (td, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.2$ Hz, 2H), 7.67–7.63 (m, 6H), 7.53 (dd, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 5.2$ Hz, 2H), 7.04–6.97 (m, 4H), 6.92 (td, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.2$ Hz), 6.39 (d, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 2.0$ Hz, 2H), 2.12 (t, $^3J_{H,H} = 8.0$ Hz, 4H), 1.15–1.02 (m, 12H), 0.79 (t, $^3J_{H,H} = 8.0$ Hz, 6H), 0.72–0.64 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): $\delta = 167.7$, 160.6, 148.7, 147.5, 145.0, 144.6, 143.6, 138.1, 134.3, 131.9, 130.4, 127.4, 124.4, 123.0, 122.7, 119.4, 59.6, 37.5, 31.6, 29.3, 24.6, 22.5, 14.1 ppm; MS (ESI+): m/z (%) calcd for $C_{45}H_{48}IrN_4$: 838.3581 $[M+H]^+$, 837.3508 $[M]^+$; found: 837.3582 (50), 837.3559 (100).

4: 4,5-Diazafluorene[32] (200 mg, 1.19 mmol) and sodium hydride (60%, 140 mg, 3.57 mmol) were dissolved in THF (40 mL), and 1,6-dibromohexane (1.84 mL, 11.9 mmol) was added in one portion. The mixture was stirred for 1 h, and the reaction was quenched with water. The solvent was evaporated, and the reaction mixture was extracted with diethyl ether and dried with $MgSO_4$. The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$ was used as eluent to remove excess 1,6-dibromohexane, and the product was flushed out with ethyl acetate) to afford pure 9,9-bis(6-bromohexyl)-4,5-diazafluorene (dC6Br-daf, **4**; 255 mg, 43%) as a colorless liquid. ^1H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 8.66$ (dd, $^3J_{H,H} = 4.8$ Hz, $^3J_{H,H} = 1.6$ Hz, 2H), 7.69 (dd, $^3J_{H,H} = 8.0$ Hz, $^3J_{H,H} = 1.6$ Hz, 2H), 7.27 (dd, $^3J_{H,H} = 8.0$ Hz, $^3J_{H,H} = 4.8$ Hz, 4H), 3.26 (t, $^3J_{H,H} = 7.2$ Hz, 4H), 2.02–1.97 (m, 4H), 1.63 (quint, $^3J_{H,H} = 7.2$ Hz, 4H), 1.17 (quint, $^3J_{H,H} = 7.2$ Hz, 4H), 1.07 (quint, $^3J_{H,H} = 7.2$ Hz, 4H), 0.68–0.60 ppm (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 25°C): $\delta = 158.2$, 149.4, 144.4, 130.4, 122.9, 51.2, 39.1, 33.9, 32.5, 29.0, 27.7, 23.9 ppm.

2: A mixture of **4** (255 mg, 0.55 mmol) and 1-methylimidazole (4.38 mL, 55 mmol) was heated to 100°C for 1 h. The reaction was quenched with water, the mixture was extracted with CH$_2$Cl$_2$, and the water layer was collected. KPF$_6$ (500 mg, 2.75 mmol) was then added to the aqueous solution, and the mixture was extracted with CH$_2$Cl$_2$. The organic layers were combined, dried with $MgSO_4$, and evaporated. The excess 1-methylimidazole was partially removed under vacuum conditions (50°C, 0.4 Torr). The crude product was used in the next step without further purification. Bis-(μ)-chlorotetrakis(2-phenylpyridinato-C^2,N)diiridium(III)[33–35] (187 mg, 0.17 mmol) and crude 9,9-bis(6-(3-methylimidazolium)hexyl)-1-yl-4,5-diazafluorene (289 mg, 0.37 mmol) were dissolved in 1,2-ethanediol (20 mL) under Ar, and the mixture was kept at 150°C for 16 h. The solution was cooled to room temperature, and an aqueous solution of NH_4PF_6 (450 mg in 5 mL deionized water) was added to yield a yellow suspension. The solid was then filtered and dried in an oven (80°C) for 1 h. The crude product was purified by column chromatography on Al$_2$O$_3$ (CH$_2$Cl$_2$/CH$_3$CN = 3:1) and then precipitated with THF and diethyl ether to afford pure **2** (350 mg, 47% over two steps) as a yellow solid. ^1H NMR (400 MHz, [D$_6$]acetone, 25°C): $\delta = 8.89$ (s, 2H), 8.34 (d, $^3J_{H,H} = 8.0$ Hz, 2H), 8.23 (d, $^3J_{H,H} = 8.0$ Hz, 2H), 7.98 (t, $^3J_{H,H} = 8.0$ Hz, 2H), 7.91

(d, $^3J_{H,H} = 5.2$ Hz, 2H), 7.87 (d, $^3J_{H,H} = 8.0$ Hz, 2H), 7.77 (d, $^3J_{H,H} = 4.4$ Hz, 2H), 7.72–7.68 (m, 6H), 7.16 (t, $^3J_{H,H} = 5.2$ Hz, 2H), 7.04 (t, $^3J_{H,H} = 8.0$, 2H), 6.92 (t, $^3J_{H,H} = 8.0$ Hz, 2H), 6.44 (d, $^3J_{H,H} = 6.4$ Hz, 2H), 4.27 (t, $^3J_{H,H} = 7.2$ Hz, 4H), 4.04 (s, 6H), 2.30 (t, $^3J_{H,H} = 7.2$ Hz, 4H), 1.82 (t, $^3J_{H,H} = 7.2$ Hz, 4H), 1.26–1.19 (m, 8H), 0.97–0.88 (m, 2H), 0.79–0.68 ppm (m, 2H); ^{13}C NMR (100 MHz, [D$_6$]acetone, 25°C): $\delta = 167.8$, 161.2, 149.7 147.9, 145.3, 145.2, 144.6, 138.9, 136.5, 135.1, 132.0, 130.2, 127.9, 124.8, 124.1, 123.7, 122.8, 122.6, 119.9, 59.8, 49.8, 37.2, 36.1, 25.8, 24.3 ppm; MS (ESI+) m/z (%) calcd for $C_{53}H_{58}IrN_8$: 999.4397 $[M]^{3+}$; found: 999.4353 (100).

Acknowledgements

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