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PAPER

Improving the balance of carrier mobilities of host–guest solid-state light-emitting electrochemical cells

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We report efficient host–guest solid-state light-emitting electrochemical cells (LECs) utilizing a cationic terfluorene derivative as the host and a red-emitting cationic transition metal complex as the guest. Carrier trapping induced by the energy offset in the lowest unoccupied molecular orbital (LUMO) levels between the host and the guest impedes electron transport in the host–guest films and thus improves the balance of carrier mobilities of the host films intrinsically exhibiting electron preferred transporting characteristics. Photoluminescence measurements show efficient energy transfer in this host–guest system and thus ensure predominant guest emission at low guest concentrations, rendering significantly reduced self-quenching of guest molecules. EL measurements show that the peak EQE (power efficiency) of the host–guest LECs reaches 3.62% (7.36 lm W^{-1}), which approaches the upper limit that one would expect from the photoluminescence quantum yield of the emissive layer (~ 0.2) and an optical out-coupling efficiency of $\sim 20\%$ and consequently indicates superior balance of carrier mobilities in such a host–guest emissive layer. These results are among the highest reported for red-emitting LECs and thus confirm that in addition to reducing self-quenching of guest molecules, the strategy of utilizing a carrier transporting host doped with a proper carrier trapping guest would improve balance of carrier mobilities in the host–guest emissive layer, offering an effective approach for optimizing device efficiencies of LECs.

Introduction

Solid-state light-emitting electrochemical cells (LECs) possess 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, giving balanced carrier injection, low operating voltages, and consequently high power efficiencies.^{1,2} As such, LECs generally require only a single emissive layer, which can be easily processed from solutions and can conveniently use air-stable electrodes, while OLEDs typically require more sophisticated multilayer structures and low-work-function cathodes.^{3,4} Compared with conventional polymer LECs that are usually composed of an emissive conjugated polymer, a salt and an ion-conducting polymer,^{1,2} LECs based on cationic transition metal complexes (CTMCs) show several further advantages and have attracted much attention in recent years.^{5–51} In such devices, no ion-conducting material is needed since these CTMCs are

intrinsically ionic. Furthermore, higher electroluminescent (EL) efficiencies are expected due to the phosphorescent nature of CTMCs.

In general, LECs are composed of neat films of emissive materials, which very often suffer self-quenching induced by interactions between closely packed molecules. Many efforts have been made to enhance device efficiencies of LECs based on CTMCs by reducing self-quenching of the emissive materials. Modifying the molecular structures such as adding bulky substituents on ligands^{9,37,41} or utilizing bulky auxiliary ligands²⁵ has been shown to suppress interchromophore interaction to some degree, improving device efficiencies of LECs. However, self-quenching is still significant in neat films even composed of materials with bulky molecular structures and thus limits device efficiencies. To further reduce self-quenching and increase EL efficiency, one feasible approach is to spatially disperse an emitting guest into a transporting host matrix, as previously reported for conventional OLEDs⁴ and solid-state LECs.^{14,26,30,36,41,45,52} Among the reported host–guest LECs, CTMCs were the most commonly used host materials and high external quantum efficiency (EQE) up to 10.4% photon/electron has been demonstrated in host–guest LECs based on CTMCs.²⁶ To optimize device efficiencies, a sophisticated molecular design for CTMC-based host materials with balanced carrier mobilities is generally required to ensure the carrier

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recombination zone to situate at the center of the emissive layer and consequently to avoid exciton quenching near electrodes⁵³ in single-layered LEC devices. Nevertheless, adjusting carrier transporting characteristics of CTMCs by modifying their ligands would simultaneously alter their energy gaps, influencing the effectiveness of energetic confinement for guest excitons when CTMCs are utilized as hosts. For instance, the neat-film photoluminescence (PL) maximum of the model compound $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]^+(\text{PF}_6^-)$ (where ppy is 2-phenylpyridine and dtb-bpy is 4,4'-di-*tert*-butyl-2,2'-dipyridyl) centers at 558 nm¹³ while the functionalized bipolar compound with dtb-bpy replaced by 4,5-diaza-2',7'-bis(diphenylamino)-9,9'-spirobifluorene, in which the 4,5-diazafluorene and diphenylamino substituents act as electron and hole transporting moieties, respectively, exhibits significant bathochromic shift in neat-film PL (maximum at 638 nm).⁴⁷ Such reduced energy gap would impede functionalized bipolar CTMCs to be used as host materials for guest materials emitting in the visible region. Furthermore, utilizing expensive phosphorescent CTMCs containing rare metals as host materials, which require a vast amount of material usage to form the emissive layer, increases the fabrication costs of LECs.

Compared with CTMC-based hosts, relatively inexpensive fluorescent polymers⁵⁴ and small-molecule materials⁵⁵ are feasible for independent tailoring of carrier transporting properties and energy gaps and thus would be more suitable for use as host materials in LECs. Host-guest phosphorescent LECs based on poly[9,9-bis(3,6-dioxahexyl)-fluorene-2,7-diyl] (BDOH-PF)⁵⁴ as the host and a red-emitting iridium complex bis[2-(2'-benzothienyl)-pyridinato-N,C^{3'}]iridium(acetylacetonate) $[\text{Btp}_2\text{Ir}(\text{acac})]$ as the guest has been reported.⁵² The host-only (BDOH-PF) LEC devices showed a high EQE up to 4%, which approaches the upper limit that one would expect from the photoluminescence quantum yield (PLQY) of the neat host films (0.73) when considering spin statistics $\sim 25\%$ for singlet excitons and an optical out-coupling efficiency of $\sim 20\%$ from a typical layered light-emitting device structure, suggesting balanced carrier mobilities in BDOH-PF neat films.⁵⁴ However, the maximum power efficiency (1 lm W^{-1}) of the host-guest LECs based on BDOH-PF doped with $[\text{Btp}_2\text{Ir}(\text{acac})]$ ⁵² was much lower than that obtained in $[\text{Btp}_2\text{Ir}(\text{acac})]$ doped OLEDs (4.6 lm W^{-1}),⁵⁶ in which multilayered structures were utilized to confine excitons in the emissive layer sandwiched between electron and hole transporting layers and thus to prevent exciton quenching near electrodes. These results reveal that when doped with guest, balance of carrier mobilities of host films would deteriorate due to carrier trapping induced by the offset in energy levels between the host and the guest and the carrier recombination zone would consequently move to the proximity of electrodes, leading to exciton quenching and thus reduced device efficiencies. Hence, to optimize the device efficiencies of the host-guest LECs, balancing carrier mobilities of the emissive layer to keep the carrier recombination zone away from electrodes would be a critical issue. In this work, we demonstrate improving the balance of carrier mobilities in host-guest LECs utilizing a cationic terfluorene derivative as the host and a red-emitting CTMC as the guest. Carrier trapping induced by the energy offset in the lowest unoccupied molecular orbital (LUMO) levels between the host and the guest impedes electron transport in the host-guest films and

thus improves balance of carrier mobilities of the host films intrinsically exhibiting electron preferred transporting characteristics. PL measurements show efficient energy transfer in this host-guest system and thus ensure predominant guest emission at low guest concentrations, rendering significantly reduced self-quenching of guest molecules. EL measurements show that the peak EQE (power efficiency) of the host-guest LECs reaches 3.62% (7.36 lm W^{-1}), which approaches the upper limit that one would expect from the PLQY of the emissive layer (~ 0.2) and an optical out-coupling efficiency of $\sim 20\%$ and consequently indicates superior balance of carrier mobilities in such a host-guest emissive layer. These results are among the highest reported for red-emitting LECs^{5-9,14,18,20,35-37,40} and thus confirm that in addition to reducing self-quenching of guest molecules, the strategy of utilizing a carrier transporting host doped with a proper carrier trapping guest would improve balance of carrier mobilities in the host-guest emissive layer, offering an effective approach for optimizing device efficiencies of LECs.

Experimental

Materials

Molecular structures of the host and guest materials used in this study are shown in Fig. 1. All compounds were synthesized according to the procedures reported in the literature.^{30,55} The cationic terfluorene derivative (**1**) reported recently by Chen *et al.* to be used in saturated deep-blue-emitting LECs was used as the host.⁵⁵ Compound **1** in dilute solutions possesses PL emission wavelengths in the deep-blue region with a high PLQY close to unity.⁵⁵ The PLQY of **1** in the form of neat films remained high (up to 0.76) despite the presence of intermolecular interactions.⁵⁵ More importantly, the addition of the ionic liquid BMIM⁺(PF₆⁻) (where BMIM is 1-butyl-3-methylimidazolium), which provides additional mobile ions in the emissive layer to fasten the device response, in the neat film did not affect the emission properties of **1**.⁵⁵ Thus, it would be suitable for use as the host material in host-guest LECs. $[\text{Ir}(\text{ppy})_2(\text{biq})]^+(\text{PF}_6^-)$ (**2**) (where biq is 2,2'-biquinoline), which was used as the red-emitting complex in white LECs reported by Su *et al.*,³⁰ was utilized as the red-emitting guest. Complex **2** exhibits saturated red PL emission in both solutions and neat films and thus is suitable for use as the red-emitting guest in host-guest LECs.

Photoluminescent characterization

Thin films for PL studies were spin-coated at 3000 rpm onto quartz substrates using mixed solutions (in acetonitrile) of

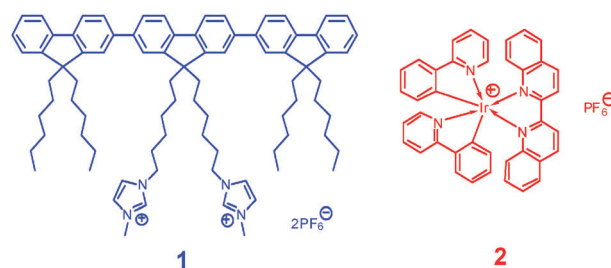


Fig. 1 Molecular structures of the host molecule, cationic terfluorene derivative (**1**) and the guest molecule, $[\text{Ir}(\text{ppy})_2(\text{biq})]^+(\text{PF}_6^-)$ (**2**).

various ratios. Since in LECs, an ionic liquid $\text{BMIM}^+(\text{PF}_6^-)$ of 10 wt% was added to provide additional mobile ions and to shorten the device response time,¹⁶ photophysical properties of the $\text{BMIM}^+(\text{PF}_6^-)$ blended host–guest films were characterized. The mass ratio of solute component [1 : 2: $\text{BMIM}^+(\text{PF}_6^-)$] in acetonitrile solutions for spin coating of the host–guest films containing x wt% guest is $(90 - x) : x : 10$. The thickness of each spin-coated film was *ca.* 200 nm, as measured using profilometry. The concentrations of all solutions for spin coating are 80 mg mL⁻¹. UV-Vis absorption spectra were recorded using a Hitachi U2800A spectrophotometer. PL spectra were recorded using a Hitachi F9500 fluorescence spectrophotometer. PLQYs for thin-film samples were determined using a calibrated integrating sphere system (Hamamatsu C9920).

LEC device fabrication and characterization

Indium tin oxide (ITO)-coated glass substrates were cleaned and treated with UV/ozone prior to use. A poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonate) (PEDOT : PSS) layer was spin-coated at 4000 rpm onto the ITO substrate in air and baked at 150 °C for 30 min. The emissive layer (~200 nm, as measured by profilometry) was then spin-coated at 3000 rpm from the acetonitrile solutions under ambient conditions. To reduce the turn-on time of the LEC device, the ionic liquid $[\text{BMIM}^+(\text{PF}_6^-)]$ (10 wt% for the host–guest devices and 20 wt% for the guest-only devices) was added to enhance the ionic conductivity of thin films.¹⁶ The mass ratio of solute component and the concentrations of solutions for spin coating of the emissive layers were the same as that used for spin coating of the host–guest films for PL studies described above. After spin coating, the thin films were then baked at 70 °C for 10 hours in a nitrogen glove box (oxygen and moisture levels below 1 ppm), followed by thermal evaporation of a 100 nm Al top contact in a vacuum chamber ($\sim 10^{-6}$ torr). The electrical and emission characteristics of LEC devices were measured using a source-measurement unit and a Si photodiode calibrated with the Photo Research PR-650 spectroradiometer. All device measurements were performed under a constant bias voltage (3.0, 3.2 and 3.4 V) in a nitrogen glove box. The EL spectra were taken with a calibrated CCD spectrograph.

Results and discussions

Photoluminescent studies of the host–guest system

PL spectra of the neat host and guest films are shown in Fig. 2. Neat films of the high-gap host (1) exhibit deep-blue fluorescent PL centered at 418 nm and yellow phosphorescent PL centered at 562 nm (the inset of Fig. 2, measured at 77 K), corresponding to a triplet energy of 2.21 eV. Neat films of the guest (2) show saturated red phosphorescent PL emission centered at 662 nm, which is equal to a triplet energy of 1.87 eV. Therefore, the triplet level of the host is higher than that of the guest and thus triplet–triplet back energy transfer from guest to host can be prevented, eliminating a potential pathway of energy loss in a host–guest system.⁵⁷ The absorption spectrum of the guest neat films is also shown in Fig. 2. Since the absorption spectrum of the guest and the PL spectrum of the host exhibit considerable

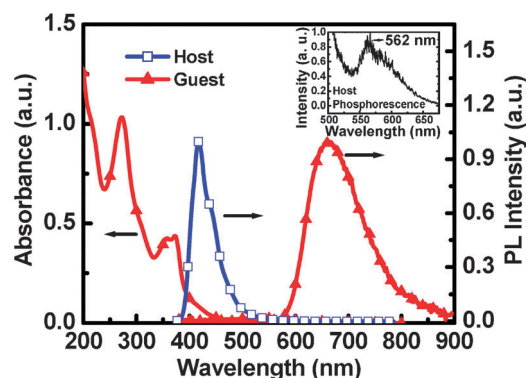


Fig. 2 Absorption spectrum of the neat guest films and PL spectra of the neat host and guest films. Inset: phosphorescence spectrum of the neat host films measured at 77 K.

spectral overlap, efficient host–guest energy transfer is expected (calculated Förster radius *ca.* 3 nm for this host–guest system) and thus the guest emission could dominate PL at low guest concentrations, resulting in significantly reduced self-quenching of guest molecules.

Fig. 3 depicts the PL spectra of the emissive layers of the host–guest LECs, *i.e.* the host–guest films containing various guest concentrations and $\text{BMIM}^+(\text{PF}_6^-)$ (10 wt%). The ionic liquid $\text{BMIM}^+(\text{PF}_6^-)$ was added to provide additional mobile ions and to shorten the device response time.¹⁶ Addition of $\text{BMIM}^+(\text{PF}_6^-)$ (10 wt%) has been reported not to affect the PL emission properties of the neat host films.⁵⁵ With the increase of the guest concentration, the relative intensity of the guest emission with respect to the residual host emission is larger due to a higher host–guest energy transfer rate at a higher guest concentration. It is noted that the PL emissions of the guest at low concentrations (0.5–2.0 wt%, Fig. 3) center at *ca.* 610 nm and exhibit significant blue shift *ca.* 50 nm as compared to those of the neat guest films (Fig. 2), indicating reduced intermolecular interactions of dispersed guest molecules in a host matrix. PLQYs of the host–guest films containing various guest concentrations and $\text{BMIM}^+(\text{PF}_6^-)$ (10 wt%) are shown in the inset of Fig. 3. PLQYs of the host–guest films decrease as the guest concentration increases from 0 to 2 wt%

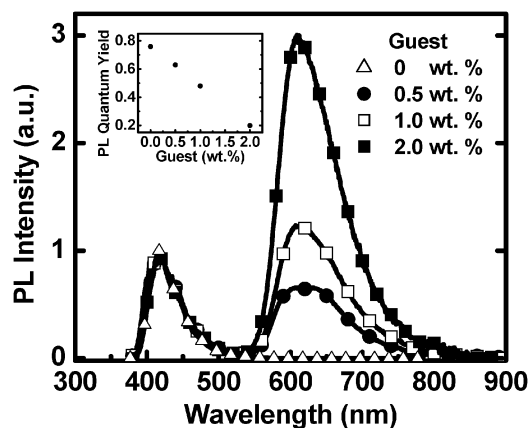


Fig. 3 PL spectra of the host–guest films containing various guest concentrations and $\text{BMIM}^+(\text{PF}_6^-)$ (10 wt%). Inset: photoluminescence quantum yields vs. guest concentrations of the same films.

since the guest emission, which exhibits a lower PLQY than the host emission, dominates PL emission at relatively higher guest concentrations. At the guest concentration of 2 wt%, most PL emission (*ca.* 90%) of the host–guest films comes from the guest and the PLQY of the host–guest films is 0.2, which is comparable with that of the guest in dilute (10^{-5} M) dichloromethane solutions.³⁰ Thus, the PLQY of the guest molecules dispersed at low concentrations in the host films would be estimated to be ~ 0.2 . Such PLQY is much higher as compared with that of the neat guest films (0.09)³⁰ and thus confirms significantly reduced self-quenching of guest molecules dispersed in the host matrix.

EL characteristics of the host–guest LECs

To clarify the EL properties of the host–guest system, EL characteristics of host–guest LECs containing various guest concentrations were measured and are summarized in Table 1. The host–guest LECs have the structure of ITO/PEDOT : PSS (30 nm)/emissive layer (200 nm)/Al (100 nm), where the emissive layer contains [host (89.5 wt%), guest (0.5 wt%) and BMIM⁺(PF₆⁻) (10 wt%)] for Device I, [host (89.0 wt%), guest (1.0 wt%) and BMIM⁺(PF₆⁻) (10 wt%)] for Device II, [host (88.0 wt%), guest (2.0 wt%) and BMIM⁺(PF₆⁻) (10 wt%)] for Device III and [host (0.0 wt%), guest (80.0 wt%) and BMIM⁺(PF₆⁻) (20 wt%)] for Device IV. The ionic liquid BMIM⁺(PF₆⁻) was added to provide additional mobile ions and to shorten the device response time.¹⁶ The EL spectra of the host–guest LECs with various guest concentrations under 3 V are shown in Fig. 4. The host–guest LECs with guest concentrations of 0.5–2.0 wt% exhibited similar saturated red EL spectra with a Commission Internationale de l'Eclairage (CIE)⁵⁸ coordinate of (0.62, 0.37). The EL spectra resemble the guest emission in the PL spectra of the corresponding host–guest emissive layers (Fig. 3), indicating similar emission mechanisms. However, the residual host emissions appeared in the PL spectra of the host–guest films are absent in the EL spectra of the host–guest LECs. These results could be understood by energy level alignments of the host and guest molecules (estimated by cyclic voltammetry)^{30,55} depicted in the inset of Fig. 4. For host–guest LECs, electrochemically doped regions of the emissive layer result in ohmic contact with metal electrodes and consequently facilitate carrier injection onto both

the host and the guest. Hence, both exciton formation on the host followed by host–guest energy transfer and direct exciton formation on the guest induced by charge trapping contribute to the guest emission. At lower biases, such energy level alignments favor electron injection and trapping on the smaller-gap guest, resulting in direct carrier recombination/exciton formation on the guest (rather than host–guest energy transfer). Thus, compared with the PL spectra (Fig. 3), the EL spectra (Fig. 4) are independent of the guest concentration and exhibit predominant guest emission even at a low guest concentration of 0.5 wt%.

The host–guest LECs with various guest concentrations exhibited similar time-dependent EL characteristics under constant-bias operation. Fig. 5(a) shows the time-dependent brightness and current density under constant biases of 3.0–3.4 V for Device I. After the bias was applied, the current first increased and then stayed rather constant. On the other hand, the brightness first increased with the current and reached the maxima of 0.13, 0.57 and 2.77 cd m⁻² under biases of 3.0, 3.2 and 3.4 V, respectively. The brightness then dropped with time with a rate depending on the bias voltage (or current). Corresponding time-dependent EQEs and power efficiencies of the same device are shown in Fig. 5(b). When a forward bias was just applied, the EQE was rather low due to poor carrier injection. During the formation of the p- and n-type regions near electrodes, the capability of carrier injection was improved and the EQE thus rose rapidly. The peak EQE (peak power efficiency) at 3.0, 3.2 and 3.4 V are 3.62% (7.36 lm W⁻¹), 2.99% (3.33 lm W⁻¹) and 2.13% (2.81 lm W⁻¹), respectively. The drop of efficiency and brightness after reaching the peak value, as commonly seen in solid-state LECs^{5–51} may be associated with a few factors. Before the device current reaches a steady value, the carrier recombination zone may keep moving closer to one electrode due to discrepancy in electron and hole mobilities, which would induce exciton quenching. Further, the decrease in brightness and efficiency under a constant bias may be rationally attributed to the degradation of the emissive material during the LEC operation.¹⁰

For comparison, time-dependent brightness/current density and EQE/power efficiency of the guest-only LECs (Device IV) are shown in Fig. 6(a) and (b), respectively. The guest-only (Fig. 6(a)) and the host–guest LECs (Fig. 5(a)) exhibited

Table 1 Summary of the host–guest LEC device characteristics

Device (guest concentration)	Bias/V	t_{\max}^a /min	L_{\max}^b /cd m ⁻²	$\eta_{\text{ext-max}}^c$ (%)	$\eta_{\text{p,max}}^d$ /lm W ⁻¹	Lifetime ^e /min
I (0.5 wt%)	3.0 V	97	0.13	3.62	7.36	527 ^f
	3.2 V	33	0.57	2.99	3.33	248
	3.4 V	11	2.77	2.13	2.81	46
II (1.0 wt%)	3.0 V	132	0.04	2.37	3.25	539 ^f
	3.2 V	78	0.59	1.74	2.15	245
	3.4 V	13	4.70	1.37	1.73	37
III (2.0 wt%)	3.0 V	131	0.02	1.01	1.18	617 ^f
	3.2 V	114	0.38	0.98	1.14	399
	3.4 V	40	3.05	0.70	0.77	102
IV (80.0 wt%) ^g	2.2 V	600	1.09	0.04	0.05	— ^h
	2.3 V	349	13.6	0.38	0.44	1221 ^f

^a Time required to reach the maximal brightness. ^b Maximal brightness achieved at a constant bias voltage. ^c Maximal external quantum efficiency achieved at a constant bias voltage. ^d Maximal power efficiency achieved at a constant bias voltage. ^e The time for the brightness of the device to decay from the maximum to half of the maximum under a constant bias voltage. ^f Extrapolated. ^g Guest-only device [mass ratio of host : guest : BMIM⁺(PF₆⁻) = 0 : 80 : 20]. ^h Extrapolation cannot be performed since brightness has not yet decreased after 10 h continuous operation.

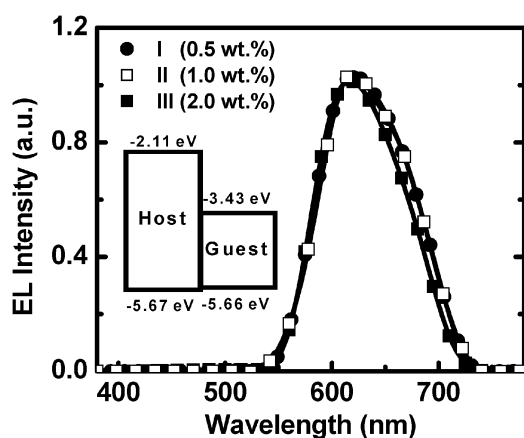


Fig. 4 EL spectra (at 3.0 V) for the host-guest LECs with various guest concentrations and $\text{BMIM}^+(\text{PF}_6^-)$ (10 wt%). Inset: the energy level diagram of the host and guest molecules.

similar characteristics in time-dependent brightness and current density. However, much larger current densities were measured in the guest-only devices even at significantly lower biases due to the lower electrochemical band gap of the guest complex **2**. The peak EQE (peak power efficiency) of the guest-only devices at 2.3 V is 0.38% (0.44 lm W^{-1}), which is much lower than that of the host-guest LECs (Table 1). Further reducing the bias voltage (2.2 V) leads to an even lower EQE (0.04%). As revealed in previous studies,¹² as bias voltage decreases, the

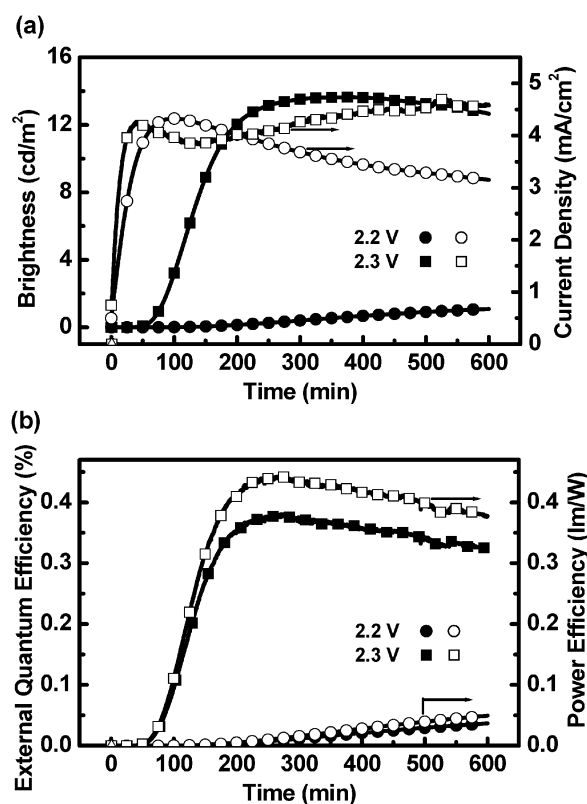


Fig. 6 (a) Brightness (solid symbols) and current density (open symbols) and (b) external quantum efficiency (solid symbols) and power efficiency (open symbols) as a function of time under a constant bias voltage of 2.2–2.3 V for Device IV.

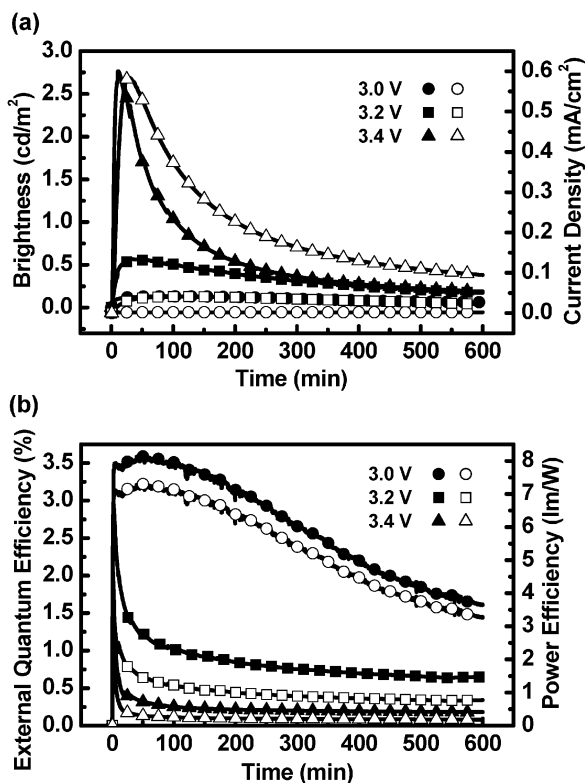


Fig. 5 (a) Brightness (solid symbols) and current density (open symbols) and (b) external quantum efficiency (solid symbols) and power efficiency (open symbols) as a function of time under a constant bias voltage of 3.0–3.4 V for Device I.

width of the intrinsic layer between the p- and n-type doped layers extends due to shrinking of the doped layers, resulting in reduced electric field in the recombination zone. Thus, reduced device efficiency under a lower bias may be attributed to deteriorated balance of carrier mobilities caused by field-dependent electron and hole mobilities.

Peak EQEs and peak power efficiencies (at current densities $< 0.003 \text{ mA cm}^{-2}$) of the host-guest LECs with various guest concentrations are shown in Fig. 7. All LEC devices contain 10 wt% $\text{BMIM}^+(\text{PF}_6^-)$ in the emissive layer. The peak device efficiency first increases then decreases as the guest concentration increases from 0 to 90 wt%. The fluorescent host-only [mass ratio of host : guest : $\text{BMIM}^+(\text{PF}_6^-) = 90 : 0 : 10$] devices show an EQE $\sim 1\%$, which is much lower than that one would expect (3.8%) from the PLQY of the neat host films (0.76)⁵⁵ when considering spin statistics $\sim 25\%$ for singlet excitons and an optical out-coupling efficiency of $\sim 20\%$ from a layered structure. Since the electrochemically doped regions near electrodes of LECs ensure balanced carrier injection,² such lowered device efficiency would be attributed to imperfect balance of carrier mobilities in the host films. As the carrier injection at both electrodes are becoming balanced, the carrier recombination zone may consequently locate near one of the electrodes due to discrepancy in electron and hole mobilities of the emissive layer. The recombination zone in the vicinity of an electrode may cause exciton quenching such that the EQE of the device would decrease. Terfluorene derivatives

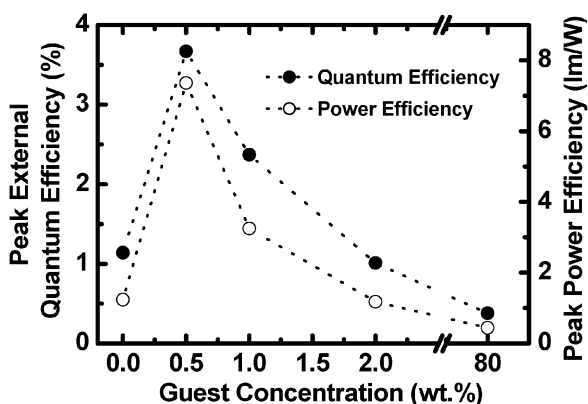


Fig. 7 Peak external quantum efficiencies and peak power efficiencies (at current densities $<0.003 \text{ mA cm}^{-2}$) of the host-guest LECs as a function of the guest concentration.

with alkyl substitutions on the tetrahedral C9 carbon have been reported to exhibit higher electron mobilities than hole mobilities.⁵⁹ Furthermore, imidazole moieties, which are tethered at the ends of the alkyl chains on **1**, have been used in electron transporting materials for OLEDs.⁶⁰ Therefore, electron preferred transporting characteristics of **1** would rationally be responsible for lowered device efficiencies of the host-only devices. The schematic diagram of the position of the exciton recombination zone for the host-only device is shown in Fig. 8(a). Since electron mobility is higher than hole mobility in the host, the exciton recombination zone would locate near the anode and thus exciton quenching occurs, deteriorating device efficiency. However, with a guest concentration of 0.5 wt%, the peak EQE (peak power efficiency) of the host-guest LECs reaches 3.62% (7.36 lm W^{-1}), which is among the highest reported for red-emitting LECs.^{5-9,14,18,20,35-37,40} It is noted that such an EQE approximately approaches the upper limit ($\sim 4\%$) that one would expect from the PLQY of the guest dispersed at low concentrations in host films (~ 0.2), when considering spin statistics $\sim 100\%$ (both singlet and triplet excitons can be harvested for a CTMC) and an optical outcoupling efficiency of $\sim 20\%$ from a typical layered light-emitting device structure. This result implies superior balance of carrier mobilities of the host-guest films with a guest concentration of 0.5 wt%. As shown in the inset of Fig. 4, balance of carrier mobilities would be significantly altered in the host-guest films due to the large energy offset (1.32 eV) in the LUMO levels between the host and the guest molecules. Electron trapping

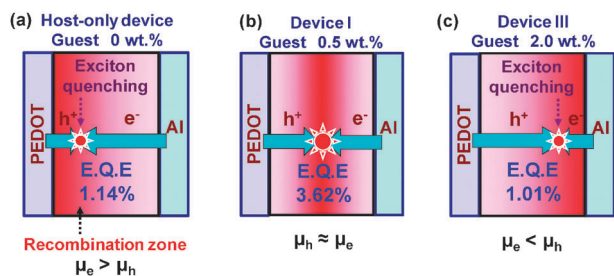


Fig. 8 Schematic diagrams of the position of the exciton recombination zone for (a) host-only device, (b) Device I and (c) Device III. Electrochemically doped regions near electrodes are omitted for clarity.

induced by the host-guest energy offset in the LUMO levels would reduce the electron mobility while the hole mobility would remain relatively unchanged due to similar energies in the highest occupied molecular orbital (HOMO) levels of the host and the guest molecules. Since the host intrinsically possesses electron preferred transporting characteristics, balance of carrier mobilities would be improved in the host-guest devices doped with an electron-trapping guest at a proper concentration. As shown in Fig. 8(b), the exciton recombination zone of the host-guest LECs with a guest concentration of 0.5 wt% would be pushed toward the center of the emissive layer due to reduced electron mobility. Thus, exciton quenching would be effectively eliminated, leading to high device efficiency. However, over-doping of the electron-trapping guest would further impede electron transporting and consequently would result in higher hole mobility than electron mobility, deteriorating balance of carrier mobilities of the host-guest films as well. Thus, with a guest concentration higher than 0.5 wt%, the device efficiency of the host-guest devices decreases as the guest concentration further increases (Fig. 7). As shown in Fig. 8(c), the exciton recombination zone of the host-guest LECs with a guest concentration of 2.0 wt% would be pushed to the proximity of cathode due to reduced electron mobility. Exciton quenching occurs again and the device efficiency is consequently low.

On the other hand, the guest-only [mass ratio of host : guest : BMIM⁺(PF₆⁻) = 0 : 80 : 20] LECs under a low bias voltage of 2.3 V exhibit a low EQE of 0.38%, which is approximately an order of magnitude lower than that achieved in the host-guest LECs doped with 0.5 wt% guest. However, the estimated upper limit of EQE of the guest-only LECs from the PLQY of the neat guest films (0.09)³⁰ when considering an optical outcoupling efficiency $\sim 20\%$ should reach *ca.* 1.8%. Thus, the low EQE obtained in the guest-only devices may be attributed to poor balance of carrier mobilities of the neat guest films. Except for a few reported LECs based on materials with balanced carrier mobilities,^{25,33,54} in which only PLQY of the emissive layer and optical outcoupling efficiency of layered device structure limits the device efficiency, balance of carrier mobilities in single-layered LECs is a common bottleneck in optimizing device efficiencies. The research results of this work confirm that in addition to reducing self-quenching of guest molecules as revealed in previous reports,^{14,26,52} the strategy of utilizing a carrier transporting host doped with a proper carrier trapping guest would also improve balance of carrier mobilities of the emissive layer and thus would be effective in optimizing device efficiencies of LECs. These device efficiencies obtained in host-guest LECs are comparable to those reported in polymer LEDs⁶¹⁻⁶⁹ and multi-layered OLEDs⁷⁰⁻⁷³ doped with iridium(III) emitters.

4. Conclusions

In summary, we have demonstrated efficient host-guest solid-state LECs utilizing a cationic terfluorene derivative (**1**) as the host and a red-emitting CTMC [Ir(ppy)₂(biq)]⁺(PF₆⁻) as the guest (**2**). Carrier trapping induced by the offset in the LUMO levels between the host and the guest impedes electron transport in the host-guest films and thus improves balance of carrier mobilities of the host films intrinsically exhibiting electron

preferred transporting characteristics. PL measurements show efficient host–guest energy transfer in this host–guest system and thus ensure predominant guest emission at low guest concentrations, rendering significantly reduced self-quenching of guest molecules. EL measurements show that the peak EQE (power efficiency) of the host–guest LECs reaches 3.62% (7.36 lm W^{-1}), which approaches the upper limit that one would expect from the PLQY of the emissive layer (~ 0.2) and an optical out-coupling efficiency of $\sim 20\%$ and consequently indicates superior balance of carrier mobilities in such a host–guest emissive layer. These results are among the highest reported for red-emitting LECs and thus confirm that in addition to reducing self-quenching of guest molecules, the strategy of utilizing a carrier transporting host doped with a proper carrier trapping guest would improve balance of carrier mobilities in the host–guest emissive layer, offering an effective approach for optimizing device efficiencies of LECs.

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