

Efficient light-emitting electrochemical cells using small molecular weight, ionic, host-guest systems

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Abstract

Light-emitting electrochemical cells (LECs) based on fluorescent host-guest small molecules system are reported. The LECs show electroluminescence coming solely from the guest, with an external quantum efficiency (EQE) of 2.0%, which is very close to the theoretical maximum EQE (2.2%) for this particular system. This work demonstrates the possibility to obtain high efficiency devices employing low-cost materials, making host-guest systems a real alternative to more traditional semiconducting polymer or transition metal compounds.

Light-emitting electrochemical cells (LECs) represent a promising alternative to more developed organic light-emitting diodes (OLEDs), especially when a simple and inexpensive device design is needed, as in the case of lighting applications. LECs employ a single active layer, either a polymer semiconductor doped with salt or a pure ionic transition metal complex (iTMC), capable

of sustaining the processes of charge injection, transport, and radiative recombination.¹⁻⁸ This unique feature arise from the presence of mobile ions in the active layer which, after biasing the device, can drift towards the electrode enhancing the charge injection.⁹ At the same time, ions stabilize the oxidation/reduction of the active material, essentially doping the semiconductor and increasing its conductivity.^{10, 11} The efficiency of fluorescent LECs is intrinsically limited by the number of singlet excitons that can lead to light-emission (~25%).^{12, 13} Phosphorescent, iTMC-based devices are able to harvest both singlet and triplet excitons, yet these suffer of severe exciton quenching due to the long lifetime of triplet states and the vicinity of the emitting species. These same issues have been solved in OLEDs by dispersing a guest triplet emitter in a charge transporting host material, resulting in efficiencies closed to the theoretical maximum value.^{14, 15} This approach requires an appropriate compatibility between the host and the guest molecule in order to allow a quantitative energy transfer between the molecular species. While a wide range of neutral hosts are commercially available, their application in LECs is limited since ionic conductors and salts need to be added to the active layers. The host-guest approach has been also applied to LECs, using a wide bandgap matrix consisting of either a blue-green emitting iTMC or a polymer semiconductor, doped with salts and fluorescent or phosphorescent dyes.¹⁶⁻²⁰ The use of iTMCs both as the host and guest materials has proved to substantially increase the device efficiency,^{17, 21} however, it limits the potential of LECs in terms of costs, due to the limited availability of metals such as iridium and ruthenium. Within this view, the development of charged semiconducting hosts for LECs remains rather unexplored. An important development was the demonstration of LECs employing simple cyanine dyes as both the charge transporting host and the light-emitting guest.²² This example is particularly interesting since it shows that LECs can be prepared using ionic low molecular weight moieties,

and also because of the large availability of the active compounds. Pertegas et al. further developed this strategy using an ionic carbazole-based charge transporting host whose bandgap is sufficiently wide to allow the excitation of a blue phosphorescent iridium complex.²³ Although high luminance level were achieved, the external quantum efficiency (EQE) was low, far from the theoretical value achievable using phosphorescent emitters. Recently, another ionic, small molecular weight carbazoyldicyanobenzene derivative (MYW2) showing thermally activated delayed fluorescence was used as the emissive layer in a LEC.²⁴ In this communication we present LECs with active layer based on MYW2 as the host to which a cyanine dye is added as the guest. Here we exploit the charge transporting properties of MYW2 and the good photoluminescence characteristics of the cyanine dye, demonstrating devices with EQE approaching their theoretical maximum value.

Materials and Methods

Acetonitrile solvent was supplied by Aldrich (HPLC grade). The host molecule MYW2 has been synthesized following a previously reported procedure.²⁴ The cyanine dye 1-Ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium hexafluorophosphate (S2108) was purchased from Few Chemicals GmbH, and used as received. Poly(methyl methacrylate) (average M_w ~120,000) was purchased in Sigma-Aldrich and was used without additional purification. Photoluminescence spectra and quantum yield (PLQY) in thin film were measured with a Hamamatsu C9920-02 Absolute PL Quantum Yield Measurement System. It consists of an excitation light source (a xenon lamp linked to a monochromator), an integrating sphere and a multi-channel spectrometer. Absorbance spectra were recorded using an Avantes Avaspec-2048 spectrometer. Both photoluminescence and

absorbance experiments in thin film were carried out on the correspondent layer deposited on a cleaned quartz plate (1x1.5cm) by spin-coating from acetonitrile solution. The LECs were made as follows. Pre-patterned indium tin oxide (ITO)-coated glass plates (Naranjo substrates) were cleaned ultrasonically in water-soap, water and 2-propanol baths. After drying, the substrates were placed in a UV-ozone cleaner for 20 min activation. An 80 nm thick layer of PEDOT:PSS (Heraeus CleviosTM P VP AI 4083) was spin-coated on the top and annealed in air at 150 °C for 15 minutes. The emitting layers (100 nm thick) was prepared by spin-coating an acetonitrile solution of the host containing 0.1 wt% of the guest molecule. After deposition of the emitting layer, the samples were transferred into a nitrogen glovebox, where the aluminum electrodes (100 nm) were thermally evaporated in a vacuum chamber through a shadow mask. The active area of the devices was 6.5 mm². All layer thicknesses were measured with a mechanical profilometer (Ambios XP-1). The devices time dependent parameters were obtained by applying a pulsed current while simultaneously monitoring the voltage and the luminance with a True Colour Sensor MAZeT (MTCSICT Sensor), using a Lifetime Test System designed by BoTEST (Botest OLT OLED Lifetime-Test System). Electroluminescence spectra were recorded with an Avantes fiber-optics photo-spectrometer. The devices were not encapsulated and were characterized inside the glovebox.

Results and Discussions

The chemical structure of the MYW2 host and of the cyanine derivative S2108 employed here as the guest emitter are reported in Fig. 1a. Previous to the incorporation into electroluminescent devices, their optical properties were evaluated. Pure thin films of the MYW2 compound show an absorption onset at about 450 nm (Fig. 1b) and a structured but continuous absorption for

lower wavelength. Note that all optical measurements on the dye have been performed on a 100 nm thick poly(methyl methacrylate) (PMMA) film doped with 1 wt% of S2108. Pure cyanine films are characterized by strongly red-shifted absorption and photoluminescence, due to extended molecular stacking.²⁵ The absorption spectra of the S2108 dye is complementary to that of the MYW2, and consists in a well-defined absorption band with maximum at 550 nm and a high energy component at 520 nm. Only a very weak band was recorded in the high energy part of the spectrum. The well separated absorption spectra of the two species is advantageous for determining if any charge transfer occurs in blends of the two materials. While exciting the MYW2 at 320 nm leads to an intense photoluminescence (PL) peak centered at 532 nm (Fig. 1c), with photoluminescence quantum yield (PLQY) of 16.2%, we were not able to detect any luminescence originating from the S2108 cyanine when exciting at the same wavelength. On the other hand, an intense, well-resolved PL spectra was obtained when exciting the cyanine at 510 nm, with a resulting PLQY of 30.2%. More interesting is the luminescence of MYW2 thin films doped with small amount (0.1 wt%) of S2108. When exciting the MYW2 host (at 320 nm), the PL spectrum of the host-guest system is dominated by the guest emission, which peaks at 568 nm with only a small contribution from the MYW2 fluorescence. This clearly shows that following optical excitation of the host, charge transfer occurs to the cyanine guest, which is promising from a device perspective. Moreover, the similarity between the photoluminescent spectrum for the host-guest and the guest dispersed in PMMA at 1wt% shows a good host-guest compatibility in the solid state. The PLQY of the mixed film is also enhanced compared to that of its component, and was found to be as high as 43.1%.

After assessing that indeed charge transfer takes place among the two molecules, their thin films were assembled into electroluminescent devices. A typical LEC architecture

ITO/PEDOT:PSS/active layer/Al, was employed. Devices were driven by applying a pulsed current at a frequency of 1 kHz and with a 50% duty cycle. This biasing mode allows for a better stabilization of the LEC functioning, in particular by reducing the turn-on time without compromising the device lifetime.²⁶ LECs were first prepared using the pure MWY2 host as the active material, in order to evaluate its charge transport properties. The devices were initially tested by applying a pulsed current density of 10 A/m² (Fig. 2a). The green electroluminescence was observed immediately (< 1 s) after biasing the LEC and the luminance kept rising steadily to reach a maximum of 13 cd/m² after about one minute. The correspondent calculated external quantum efficiency (EQE, Fig. 2c) reached a maximum of 0.4%; taking into account the PLQY of the MWY2, the singlet exciton generation yield (25%), and an out-coupling efficiency of 20%, the recorded peak EQE is half of the theoretical maximum value achievable (~0.8%). Since the rather low maximum luminance obtained depends on the applied current density, we tried to increase it by biasing the device at 25 A/m². While the luminance was indeed augmented, a diminution of the correspondent device EQE was also observed (Fig. 2b-c). For all the applied current densities, the measured bias (Fig. 2a) shows a profile typical for LECs, with high voltage in the beginning of the measurement slowly converging towards values corresponding to the bandgap energy of the organic material. This trend is a consequence of the ionic redistribution within the active layer, which in turn redistributes the field at the electrode interfaces enhancing charge injection. A voltage as low as 2.7-2.8 V was observed after biasing for about 10 minutes, meaning that no barrier for charge injection is present at this operating time. The corresponding low EQE can be due to exciton quenching by the proximity of an electrode interface, caused by unbalanced electron/hole transport in the material. This hypothesis is supported by the partially

irreversible oxidation wave observed in cyclovoltammetry of the MYW2 host, and also by the limited device lifetime.²⁴

We then examined the behavior of an analogous LEC employing the host-guest system, using 0.1 wt% of the cyanine dye into the MYW2 matrix. The device performances are summarized in Fig. 3. Yellow electroluminescence was observed immediately after biasing the LEC, independently on the current density applied. The device biased at 10 A/m^2 showed a maximum luminance of 65 cd/m^2 within a minute of operation (Fig. 3b). Such brightness is modest but still represents a five-fold increase when compared to the pure host. With increasing current density (25 A/m^2) the electroluminescence changed substantially, with a maximum luminance of 165 cd/m^2 immediately after biasing the device. In terms of efficiency, LECs employing the host-guest system as the active layer showed a maximum EQE of 1.90% (Fig. 3c), independently on the excitation intensity. Taking into account the thin-film PLQY of the S2108 dye doped into the MYW2 host (43.1%), and considering the singlet generation yield and out-coupling efficiency, the maximum theoretical value is only slightly higher than the measured EQE, about 2.16%. This result is of great interest for future applications of LECs, since it confirms that the host-guest approach widely applied to OLEDs would also be valid in the case of much simpler devices such LECs. It is interesting to note that the electroluminescence spectrum of the host-guest system (Fig. 4) shows a single peak centered at about 571 nm while it lacks the component originating from the matrix previously observed in photoluminescence (Fig. 1c). This implies that photon generation is coming solely by the cyanine host, and hence that the charge transfer via either Förster energy transfer or sequential trapping from the MYW2 host to the S2108 guest is responsible for the enhanced efficiency.

Conclusions and Outlook

The optoelectronic properties of ionic host-guest systems based on a charged carbazole derivative doped with a cyanine dye were investigated. This configuration mirrors the approach used in high efficiency OLEDs, where a wide bandgap host material is doped with the guest chromophore, and charge transfer occurs between the two species. The system presented here exhibits efficient charge transfer from the host to the guest when optically excited, and the quantum yield for luminescence is substantially increased compared to either the individual materials. Notably, the charge transfer is also observed in electroluminescence, and the overall device efficiency is only slightly below its maximum theoretical value. These observations pave the way for a renewed development of LECs, in particular in terms of material research for appropriate host-guest molecular systems. Furthermore, the idea can be applied to similar higher band-gap host materials in order to cover a wider range of visible region. Future work should not neglect the investigation on the origin of the limited device lifetime, which is a prerequisite for a potential impact of LECs in the lighting market.

Figures

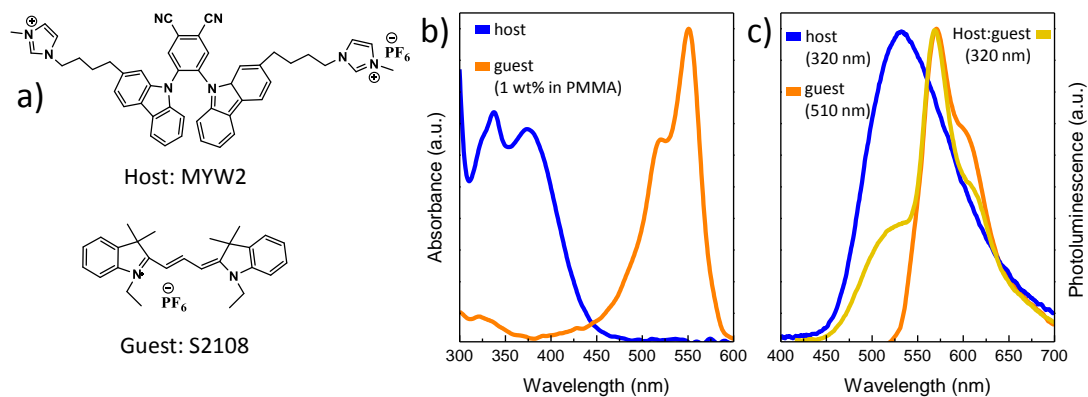


Figure 1. Chemical structure (a), thin film absorption (b) and photoluminescence spectra (c) for of the host and guest compounds. For recording both spectra, the S2018 guest molecule was dispersed in PMMA. The numbers in parenthesis in (c) indicates the excitation wavelength.

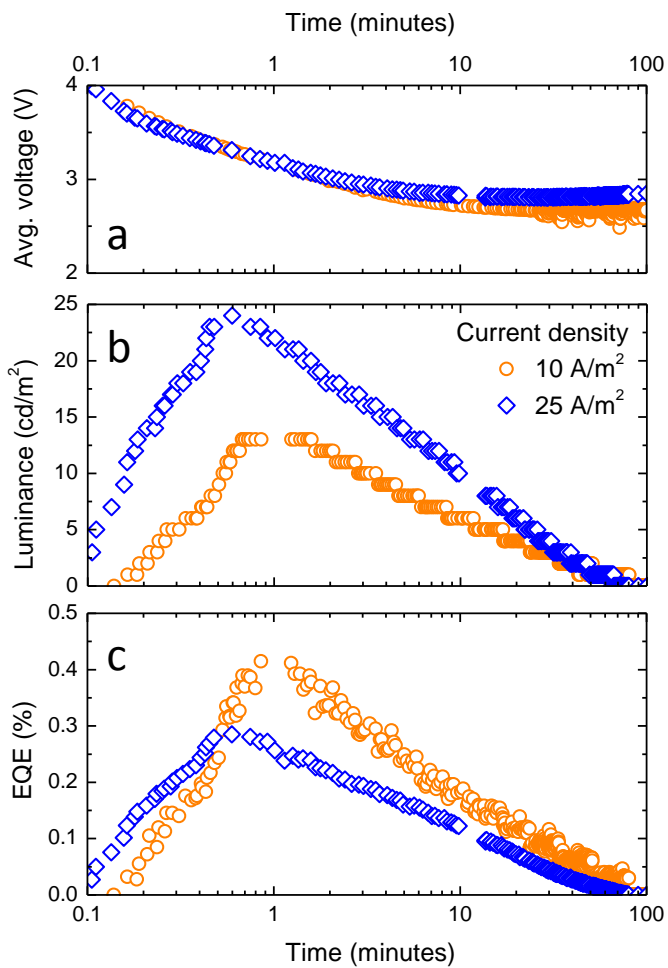


Figure 2. Dynamic behavior of LECs employing the pure MYW2 host as the active layer. Average voltage (a), luminance (b) and EQE (c) are reported as a function of time and for different applied current densities.

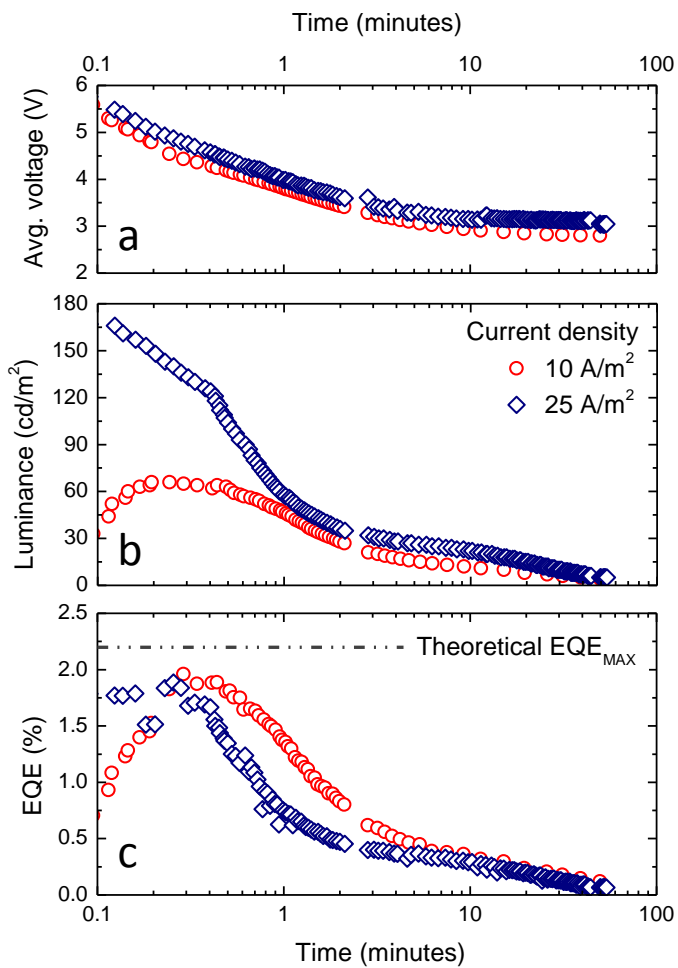


Figure 3. Dynamic behavior of LECs employing the host-guest (MYW2 doped with S2018 at 0.1 wt%) system as the active layer. Average voltage (a), luminance (b) and EQE (c) are reported as a function of time and for different applied current densities. In (c), the dotted line represents the theoretical limit of the EQE for this particular system and device.

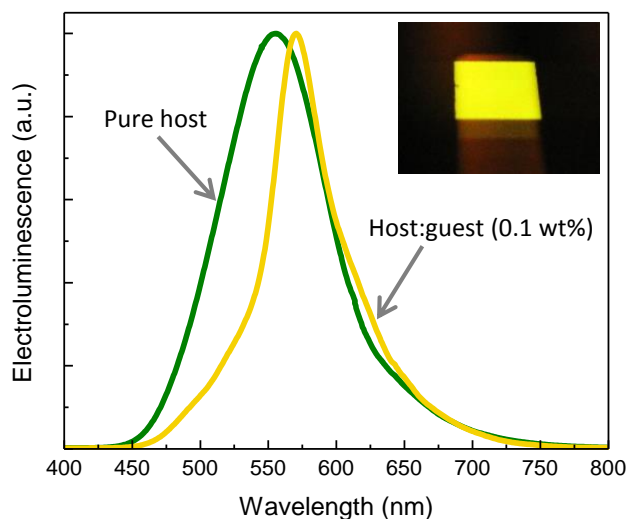


Figure 4. Electroluminescence spectra measured for LECs using the pure host (green) and the host-guest system as the emissive layer. The inset shows a photograph of a working host-guest pixel.

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