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Light-Emitting Electrochemical Cells Using Cyanine Dyes as the Active Components

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Supporting Information

ABSTRACT: Light-emitting electrochemical cells (LECs) based on cyanine molecules were prepared. High photoluminescence quantum yields were obtained for host–guest films using two cyanine dyes, reaching 27%. Sandwiching these films in between two electrodes allows for very stable near-infrared emission with a maximum radiant flux of 1.7 W m^{-2} at an external quantum efficiency of 0.44%.

Two decades ago Pei et al. introduced a polymer light-emitting diode admixed with ions showing attractive properties like a strongly reduced dependence on the active layer thickness and a bipolar charge carrier injection from stable electrode materials such as Au: the polymer light-emitting electrochemical cell (pLEC).[1,2] A year later, an alternative was reported using an ionic transition-metal complex (iTMC) as the active material.[3] Both types of LECs have reached quite promising performances,[4,5] and can be roll-to-roll processed.[6] In particular, high stabilities and efficiencies have been reported for iTMC-based LECs.[7,8] Recently, it has been shown that, independently of the class of materials employed, polymers or iTMCs, the devices operate in a similar fashion that depends primarily on the conductivity of the ions in the composition.[9] Ir-iTMC-based LECs show the best performances, reaching high efficiencies (36.8 lum W^{-1}) and stabilities (>5000 h at a starting luminance >600 cd m^{-2}), albeit not in one single device.[7,10] Nevertheless, the low abundance and elevated cost of iridium may lead to high materials cost for Ir-iTMC-based LECs, impeding their use in large-scale low-cost applications. Therefore, it is of interest to identify other materials that may lead to efficient LECs. Recently, it was shown that small molecules, when combined with polyethyleneoxide and a salt, can be used as the active layer in a LEC.[11] This alternative increases tremendously the number of materials exploitable in LECs. However, it requires a tricomponent blend, whereas an ionic emitter such as the Ir-iTMC is the only active component leading to simpler film architectures and morphologies. This is important to allow for reproducible processing on roll-to-roll techniques.

Therefore, efficient ionic emitting materials are of interest especially if they are able to transport electronic charges. Cyanine dyes (a class of polymethine dyes) are ionic compounds that have been used in applications such as photography and photodynamic therapy, laser materials, light-harvesting systems in photosynthesis and photovoltaics, photorefractive materials, optical data storage, and organic solar cells, and are widely available at low cost.[12,13] Their use in organic solar cells, where they function as the absorber and as the electron donor or, depending on the configuration, as the electron acceptor, is of special interest.[14,15] In these photovoltaic cells, electrons and holes are collected at the external electrodes by transport through the cyanine dyes demonstrating their charge transporting capabilities. Hence, cyanine dyes are ionic, strongly luminescent, and capable of transporting electrons and holes making them possible candidates for applications in LECs. Additionally, cyanine dyes are processable from benign solvents, which adds to the ease of thin film preparation.

Here we present a LEC based solely on cyanine dyes as the active components. A two-component emitting layer consisting of a cyanine dye host and a cyanine dye emitter is developed to prevent exciton quenching and emission losses. Due to the intrinsic ionic nature of the dyes, no additional salt is needed. The performance of these near-infrared emitting LECs is very promising, showing a radiant flux of 1.7 W m^{-2} and an efficiency of 0.44%. This is an important achievement as it demonstrates that ionic fluorescent molecules can yield, like the ionic phosphorescent molecules, efficient electroluminescence without additional components and without the need for rare heavy metals.

LECs devices were prepared on ITO-covered glass substrates (www.naranjosubstrates.com) employing a poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, (HEREAUS, Clevios AI4083)) layer of 80 nm prior to the deposition of the active materials. The light-emitting layer (80 nm) consisted of the dye or a blend of two dyes. Two cyanine dyes were selected based on their emission spectra and fluorescent quantum yield in dilute solutions: 1-ethyl-2-[3-(1-ethyl-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)-propenyl]-3,3-dimethyl-3*H*-indolium hexafluorophosphate (dye **H**, Figure 1) and 1-butyl-2-[5-(1-butyl-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)-penta-1,3-dienyl]-3,3-dimethyl-3*H*-indolium hexafluorophosphate (dye **G**, Figure 1). Both dyes were obtained from FEW chemicals and used as received. Aluminum was employed as the top cathode. Estimates of the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO, respectively, for both dyes (Figure 1) were obtained by quantum chemical calculations (see Supporting Information).

LECs were first prepared using the orange emitter **H** as the unique active component and operated using a constant bias of

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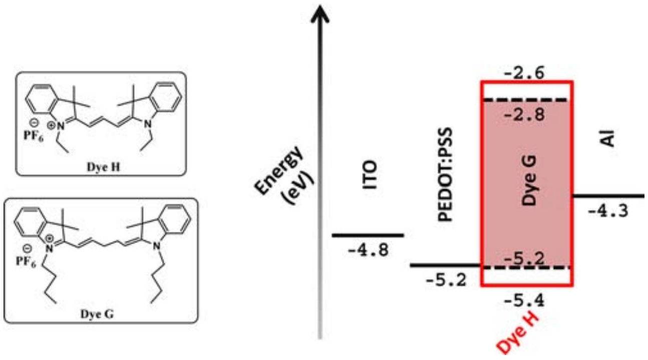

Figure 1. Schematic of the energy levels of the materials used in the LEC and the chemical structures of the cyanine dyes **H** and **G**.

3 V. The performance observed is typical for LECs, showing a slow increase in the current density and radiance over time (Figure 2).[9] This slow rise in current density and subsequently in luminance is due to the slow ionic movement in the active film.

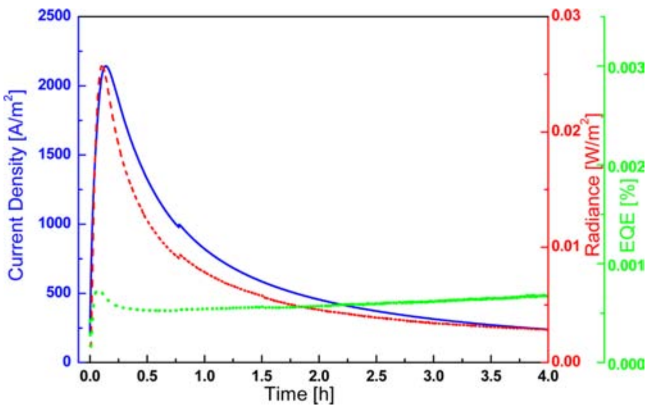

Figure 2. Current density (blue), radiant flux (red), and EQE (green) versus time for ITO/PEDOT:PSS/Dye **H**/Al at 3 V.

Due to the large energy difference between the work function of the electrodes and the energy of the HOMO and LUMO of the dye, electron and hole injection does not occur at 3 V. It requires the accumulation of ions at the interface to reduce the injection barriers for electrons and holes.[16] In view of the calculated size of the dyes (**H**, 487; and **G**, 608 Å^3) versus that of the counterion PF_6^- (107 Å^3), it appears the latter is the more mobile one. The rapid decrease in current density and luminance after the maximum has been reached is also typical for constant voltage driven LECs. This is partially due to charge and exciton trapping but is also due to permanent degradation.[17] The radiance of this LEC is, however, rather low due to the low photoluminescence quantum efficiency (PLQE), which is <1% for thin films consisting of only dye **H**. In a solid film, excitons can hop from one dye molecule to another and eventually encounter quenching sites. As a result, the external quantum efficiency (EQE) of these LECs is rather poor reaching only 0.001%. Yet, the current densities are high indicating that electrons and holes are efficiently transported through the layer.

Hence, to increase the performance of these LECs, the PLQE must be improved. This is possible if a smaller bandgap emitter is dispersed in a wider bandgap host. This concept has been used successfully in organic light-emitting diodes (OLEDs) and also in Ir-iTMC-LECs leading to high efficiency devices.[10] The excitation of the guest occurs via either Föster energy transfer from the host to the guest or sequential trapping of charge carriers on the guest. Here, we have adopted the same approach by dispersing the cyanine dye **G** in a matrix of cyanine dye **H**. These dyes were chosen as the absorption band of dye **G** overlaps with the emission band of dye **H**. To determine the optimum concentration of dye **G** in the matrix of dye **H**, the photoluminescence spectra and PLQEs were determined for different blends while exciting at a fixed wavelength of 526 nm which corresponds to one of the absorption bands of dye **H** (Figure 3). Pure films of dyes **H** and **G** did not lead to detectable photoluminescence. The solution photoluminescence spectra of **H** and **G**, recorded in deaerated acetonitrile solution (~10^{-5} M) (an excitation wavelength of 595 nm was used for dye **G**), are included in Figure 3 for comparison purposes. In the range evaluated (0.1–2.5% wt), all films show strong emission at 700 nm corresponding to the emission of dye **G**. The films with **G** concentrations above 0.1% wt show an increasing emission originating from the second emission peak located around 750 nm. Additionally, the highest PLQE (27%) was observed for the film with the lowest amount of dye **G** (0.1% wt). For this reason, we selected the film containing 0.1% wt of dye **G** in a matrix of dye **H** for further evaluation in LECs.

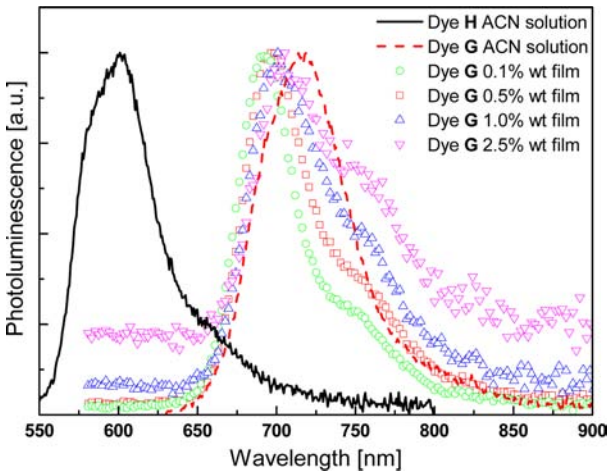

Figure 3. Photoluminescence (PL) spectra of dyes **H** and **G** in acetonitrile solution and mixtures of dye **H**:dye **G** at different ratios (0.1–2.5% wt) in solid state.

To evaluate the electroluminescent behavior of LECs based on the cyanine Host:Guest film with 0.1% wt of dye **G** in dye **H**, these films were used to prepare LECs in the same way as described above. The electroluminescent spectrum of these LECs shows a maximum emission at 706 nm, which undoubtedly corresponds to the emission of dye **G** (Figure S1). No residual electroluminescent emission from the host was detected in accordance with PL studies described above.

The time response of the cyanine-based Host–Guest LECs is depicted in Figure S2 and Figure 4. When constant voltage driving is used, best peak performances are obtained yet they are not stable in time. More stable performance and faster turn-on can be obtained when a current driving,[18] or preferably a pulsed driving protocol is applied.[7] Figure 4 shows the average voltage, the radiance, and the EQE for two host–guest LECs operated under a pulsed current of 100 A m^{-2} using a block-

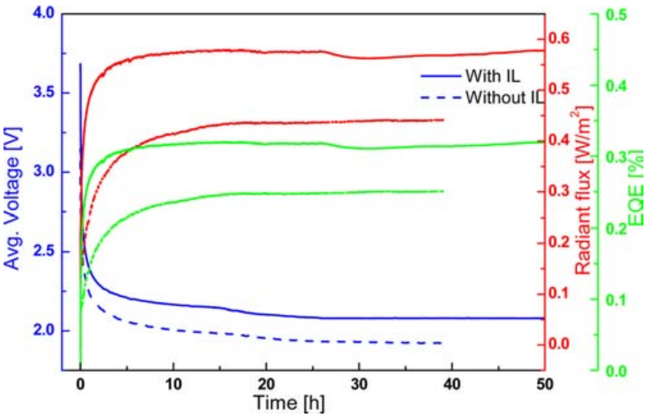

Figure 4. Average voltage (blue), radiant flux (red), and EQE (green) versus time for an ITO/PEDOT:PSS/Matrix/Al LEC operated under a pulsed current of 100 A m^{-2} using a block-wave at 1000 Hz and a duty cycle of 50%. Dashed line: Matrix = dye **H** + 0.1% wt of dye **G**. Solid line: Matrix = dye **H** + 0.1% wt of dye **G** + 16.7% wt of (1-butyl-3-ethylimidazolium hexafluorophosphate).

wave at 1000 Hz and a duty cycle of 50%. The average voltage required to apply the 100 A m^{-2} rapidly reduces with time. At the same time, the radiance increases to reach a maximum value, after which it remains virtually constant for more than 100 h. The EQE follows the radiance curve and also is very stable over time. Devices to which some extra ions in the form of the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate were added showed a slightly higher radiance and EQE.[9,19−22]

Considering the PLQE of 27% and an outcoupling typically of 20%, the theoretical EQE for a LEC based on a fluorescent emitter is 1.3% when all injected electrons and holes combine. We observe an EQE for the best device of 0.44%, which is roughly one-third of the theoretical maximum. Taking into account that no optimization of electron and hole transport has been performed, this is a remarkably good figure. Recently, near-infrared LECs were reported that use cyanine dyes as the emitter in a host of Ir-iTMCs. In those LECs, EQEs around 1% were reported yet at rather low radiances (<80 mW m^{-2}).[23] High-efficiency near-infrared OLEDs using a phosphorescent platinum complex in an evaporated device stack yielded a maximum EQE of 6% at a radiance of 1 mW m^{-2}.[24] The same device, when driven at higher voltage, showed a radiance of 7 W m^{-2}, yet under these conditions, the EQE was reduced to 0.6%. In another recent work, PbS quantum dots were employed as the light-emitting material.[25] Again, our results are comparable in terms of the combination of radiance, wavelength, and EQE. The lifetime curve (although only over a limited time frame) of our devices is comparable with that reported for the near-infrared OLED described above that suffers a luminance decrease of 10% over the first 1000 h.

To conclude, we have shown that a well-known class of materials, cyanine dyes, can be used to prepare efficient near-infrared light-emitting devices that emit high radiance levels. Due to the ionic nature of the dyes, the devices operate according to the mechanism established for light-emitting electrochemical cells, allowing the use of air-stable electrodes and very low operation voltages. High performances are only obtained when two dyes are used, in a host−guest configuration. This is needed to increase the photoluminescence quantum yield of the active film. As cyanine dyes are easily adjusted and prepared in large quantities, they constitute an interesting class of ionic emitting materials to be further evaluated in solution-processed light-emitting devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The emission spectrum of the host−guest LEC, the device performance under constant voltage and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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