Electronic Supplementary Information (ESI)

Small-Molecule Light-Emitting Electrochemical Cells: Evidence for *In-situ* Electrochemical Doping and Functional Operation

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LEC operation

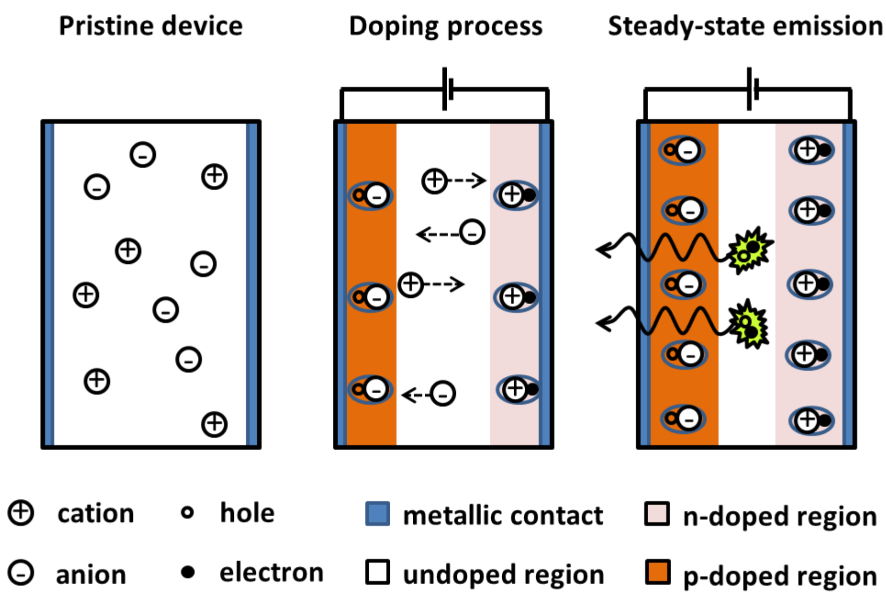

Figure S1. *Schematic presenting the constituent processes during the turn-on of an LEC device.*

Light-emitting electrochemical cells (LECs) are distinct from the more commonplace organic light-emitting diode (OLED) *via* the existence of mobile ions in the active layer. When a voltage is applied over the two electrodes in an LEC, these mobile ions redistribute to form electric double layers (EDLs) at the two electrode interfaces. When a sufficiently high voltage is applied ($V \geq E_g/e$; where E_g is the energy gap of the SM, and e is the elementary charge), these EDLs assist with the efficient and balanced injection of electrons and holes at the cathodic and anodic interfaces, respectively. The injected electronic charge carriers subsequently attract electrostatically compensating ions in an electrochemical doping process, being n-type at the cathode and p-type at the anode. With time, these electronically conducting doping regions grow in size to eventually make contact under the formation of a light-emitting p-n junction in the bulk of the active layer. Figure S1 presents a schematic of the *in-situ* formation of a p-n junction doping structure in an LEC device. It is clear that the redistribution of bulky ions during the EDL formation and the subsequent electrochemical doping process are time consuming processes in comparison to, *e.g.*, the solely electronic processes in effect during the turn-on of an OLED, which rationalizes the second-long turn of the LEC devices presented in Figs. 2 and 3a in the main manuscript.

Experimental Section

The electroactive and emissive small molecules (SMs) 4-(3,5-di(4-*sec*-butoxyphenyl)phenyl)-7-(7-(3,6-di(1-naphthyl)carbazol-9-yl)-9,9-di-*n*-octylfluoren-2-yl)-2,1,3-benzothiadiazole[1] and 4,7-bis(4-(4-*sec*-butoxyphenyl)-5-(3,5-di(1-naphthyl)phenyl)thiophen-2-yl)-2,1,3-benzothiadiazole[2] are termed "Green" and "Red", respectively, for convenience; their synthesis have been reported previously.[1, 2] The salts KCF_3SO_3 (Aldrich) and $LiCF_3SO_3$ (Aldrich), the ionic solvents poly(ethylene oxide) (PEO, $M_w = 5\times10^6$ g/mol, Aldrich) and trimethylolpropane ethoxylate (TMPE, M_w = 450 g/mol, Aldrich), and poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, Clevios P VP AI 4083, Heraeus) were used as received. Master solutions with a concentration of 20 g/l were prepared. Blend solutions were prepared by blending the master solutions in a desired mass ratio. Master and blend solutions were vigorously stirred for 6 h at T = 50 °C before further processing. Indium-tin-oxide (ITO) coated glass substrates (1.5×1.5 cm^2, 20 Ω/square, Thin Film Devices) and glass substrates (1.5×2.5 cm^2) were cleaned by subsequent ultrasonic treatment in detergent, acetone, and isopropanol.

Bilayer planar LECs were fabricated by sequentially spin-coating the glass substrates with 10 g/l {PEO+KCF_3SO_3} in acetonitrile (at 800 rpm for 60 s) and 20 g/l SM in THF (at 2000 rpm for 60 s). The mass ratio of the electrolyte constituents was PEO:KCF_3SO_3 = 1.35:0.5, and the dry thickness of the electrolyte/SM bi-layer was 180/120 nm. Au electrodes were deposited on top of the bi-layer by thermal evaporation under high vacuum ($p < 2\times10^{-6}$ mBar); the inter-electrode gap of 120 µm was established using a shadow mask. Sandwich cells were fabricated by sequentially spin-coating ITO-coated glass substrates with PEDOT-PSS (at 4000 rpm for 60 s) and {SM:TMPE:$LiCF_3SO_3$} active material (at 2000 rpm for 60 s); the mass ratio of the active layer components was SM:TMPE:$LiCF_3SO_3$ = 1:0.15:0.06 (SM = Red) and 1:0.10:0.06 (SM = Green). The dry thickness of the PEDOT-PSS/active-material bi-layer was 40/120 nm. Al cathodes were deposited on top of the active material by thermal evaporation through a shadow mask yielding an emission area of 0.85×0.15 cm^2 for each of 4 devices on one substrate. All of the above procedures, except the cleaning of the substrates and the spin-coating of PEDOT-PSS, were carried out in two interconnected N_2-filled glove boxes ([O_2] < 3 ppm, [H_2O] < 0.5 ppm).

The characterization of planar LECs was performed under vacuum ($p < 5\times10^{-5}$ mBar) in an optical-access cryostat. A computer-controlled source-measure unit (Keithley 2400) sourced voltage and measured current. The photographs of the doping process and light emission were recorded under UV illumination (λ = 365 nm) through the optical window of the cryostat, using a digital camera (Canon EOS 50D) equipped with a macro lens (65 mm, F/2.8). The characterization of sandwich-cell LECs was executed in a glove box, using a computer-controlled source-measure unit (Agilent 2722A), a calibrated photodiode equipped with an eye-response filter (Hamamatsu Photonics), and a fibre-optic spectrometer (USB2000, Ocean Optics). The CIE coordinates were calculated using the SpectraWin software.

Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation. A platinum microdisc was used as the working electrode, platinum filament was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The electrolyte comprised 0.1 M Bu_4NPF_6 dissolved in a nitrogen-saturated solution of CH_2Cl_2 and CH_3CN (5:1 ratio). The mixed solvent system was employed in order to observe reversible redox waves. The SM under study was dissolved in the electrolyte solution. Directly after each (cathodic or anodic) CV scan, a calibration scan was run with a small amount of bis-(η-cyclopentadienyl)iron(II) (ferrocene, ≥98%; Fluka) added to the electrolyte. All potentials in the CV measurements are reported versus the ferrocene/ferrocenium ion (Fc/Fc^+) reference redox system. The scan rate was 50 mV/s, and the onset potentials for oxidation and reduction were calculated as the intersection of the current baseline with the tangent of the current at the half-maximum of its peak value.

Results

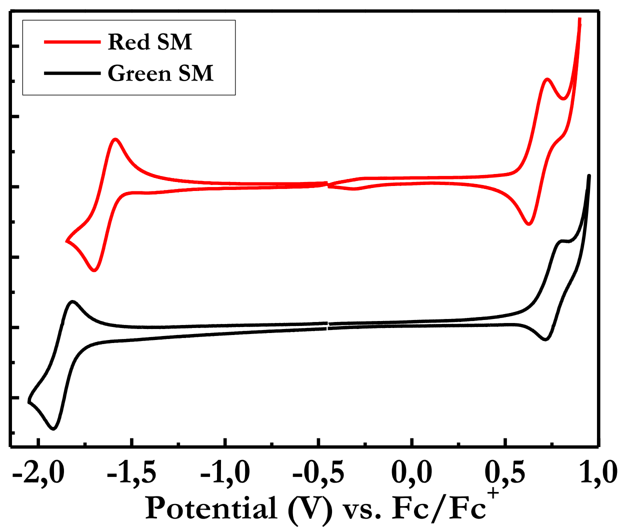

Figure S2*. Cyclic voltammetry data for the Red and Green SM.*

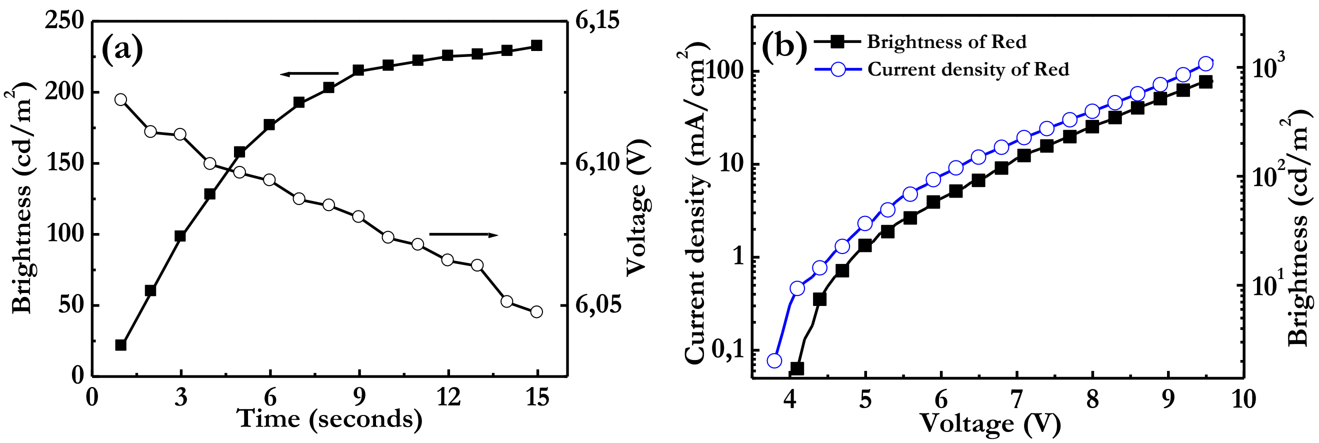

Figure S3. *Optoelectronic response for an ITO/PEDOT-PSS/{Red+TMPE+$LiCF_3SO_3$}/Al sandwich cell. (a) Turn-on kinetics during galvanostatic operation at j = 38.5 mA/cm^2. (b) Current density and brightness as a function of voltage during a voltage scan at dV/dt = 0.1 V/s.*

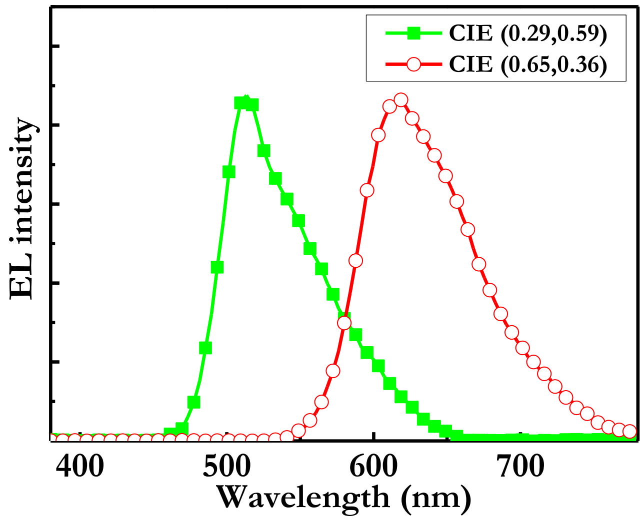

Figure S4. *Normalized EL spectra of sandwich-cell LECs with Red as the emitter (red open circles) and Green as the emitter (green solid squares). The inset indicates the corresponding CIE coordinates.*

References

1. Y. Li, A.-Y. Li, B.-X. Li, J. Huang, L. Zhao, B.-Z. Wang, J.-W. Li, X.-H. Zhu, J. Peng, Y. Cao, D.-G. Ma and J. Roncali, Org. Lett., 2009, 11, 5318-5321.
2. J. Huang, Q. Liu, J.-H. Zou, X.-H. Zhu, A.-Y. Li, J.-W. Li, S. Wu, J. Peng, Y. Cao, R. Xia, D. D. C. Bradley and J. Roncali, Adv. Funct. Mater., 2009, 19, 2978-2986.