Doping Evolution and Junction Formation in Stacked Cyanine Dye Light-Emitting Electrochemical Cells

Empa
Materials Science and Technology

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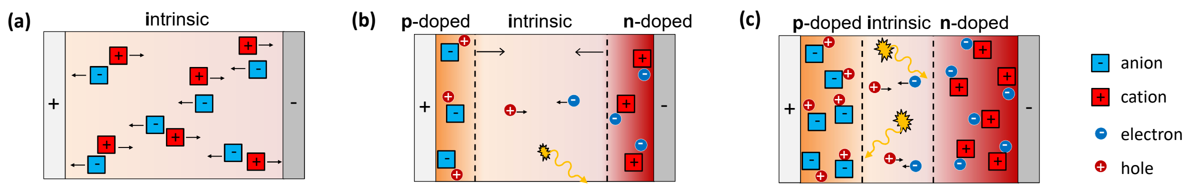
Introduction

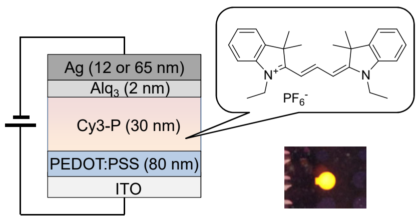
Organic light-emitting electrochemical cells (LECs) were invented as an easy-to-fabricate and electrode-insensitive alternative to the more famous organic light-emitting diodes (OLEDs). The emissive layer is a semiconducting material that has to be able to transport both ionic and electronic charges. Their peculiar operation mechanism is explained by the electrochemical doping (ECD) model. Upon applying a voltage the ions drift to the respective electrode **(a)** where they facilitate electronic charge injection. This causes p- and n-doped regions that grow towards each other with time **(b)**. Light emission originates from the central intrinsic region where electronic charges recombine radiatively **(c)**.



Results

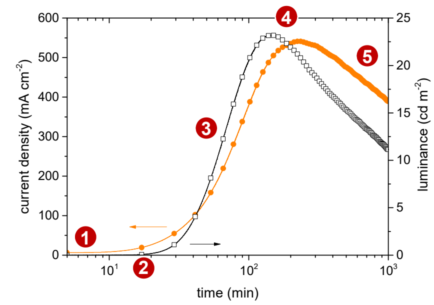
Materials and device structure

- The active component is a trimethine cyanine dye with a mobile PF_6^- counter ion (Cy3-P)
- The emission of the final device is orange (see photograph)



Operation mechanism

- A typical luminance and current transient for constant 3V operation is shown below

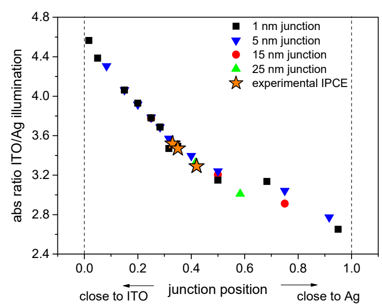


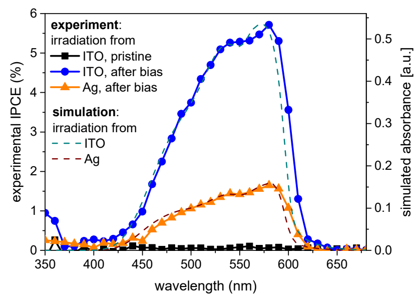
- The behaviour of all points in time (1-5) are explained by the ECD model:

1. Ions drift to the electrode
2. Charges are injected and start to recombine causing light emission to start
3. Doped regions grow increasing current and luminance
4. Doped regions grow further which deteriorates the luminance because of too much exciton quenching
5. Unspecific degradation of the active material

Junction position determination

- The developed p-i-n structure is able to split excitons thus we can measure its photovoltaic response
- As p- and n-doped regions quench excitons the extracted charge originates from the intrinsic region only
- A semi-transparent Ag electrode enables to measure IPCE with illumination through either ITO or Ag
- Optical simulations for the full device dividing the active layer in a p-, n- and an i-region have been performed to determine the intrinsic layer absorption
- The ratio of the simulated intrinsic layer absorption through both illumination sides can directly be compared to the ratio of the experimental IPCE

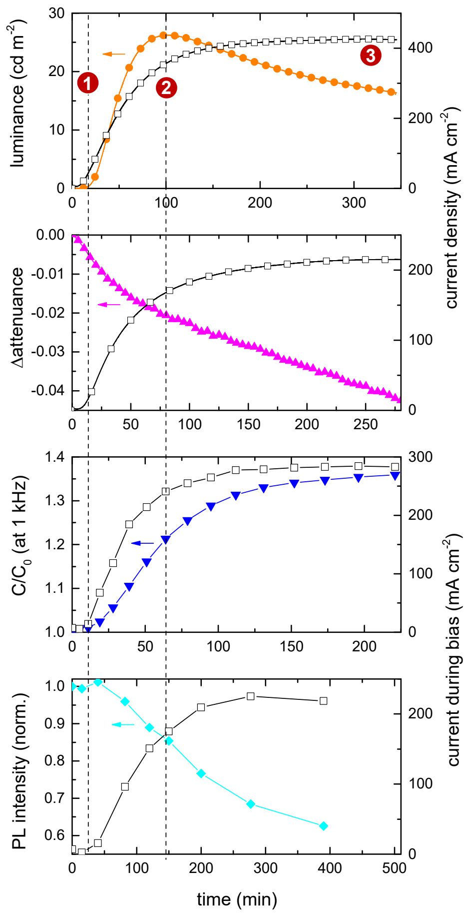




- Simulated absorption ratios do not depend on the thickness of the intrinsic region
- The centre of the junction was determined to be ~37% of the total Cy3-P layer away from the ITO contact

Dynamic doping and junction evolution

- Luminance + Current: Follow the state of the LEC
- Absorption: The cyanine monomer species is consumed to form n- and p-doped species. In the absence of side reactions this decrease is equal to the sum of all dopants.
- Capacitance: As the doped regions are highly conductive the device capacitance is given by the intrinsic region.
- Photoluminescence (PL): Doped regions do not show PL because excitons are quenched. Thus the remaining PL enables us to calculate the thickness of the intrinsic region.

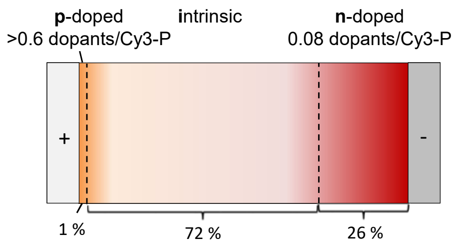


Parameter	1	2	3
Doping conc.		2.6 ± 0.6 %	4.4 ± 1.7 % *
d_{int} (from cap.)	99 % (of d_0)	83 % (of d_0)	72 % (of d_0)
d_{int} (from PL)	100 % (of d_0)	85 % (of d_0)	65 % (of d_0)

* Using d_{int} and the junction position individual n- (0.08) and p-doping (>0.6) concentrations can be calculated.

Conclusions

- Cyanine dye is used as active component in an LEC
- IPCE and optical simulation was used to determine the centre of the junction to be at ~37% of the total Cy3-P layer away from the ITO contact
- Transient luminance, attenuance, capacitance and PL signals were used to estimate doping concentrations and calculate junction layer thicknesses for every point during operation
- Together, these data give a full picture of the operating device (sketch on the right illustrates the situation at maximum current)



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