POLYMER LIGHT-EMITTING ELECTROCHEMICAL CELLS (PLECs):

Scanning Optical Beam Induced Current (OBIC) and Photoluminescence (PL) Imaging

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- ➢ Polymer Light-emitting Electrochemical Cells (PLECs).

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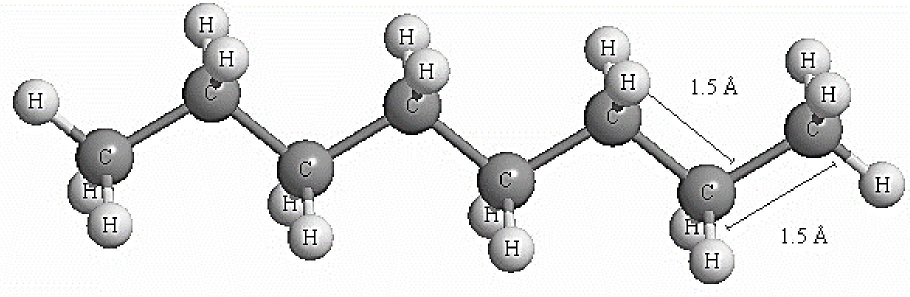
Polymers

❑ Saturated polymers:

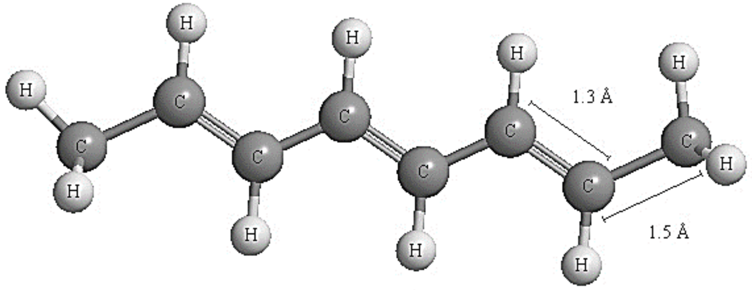
- ➢ Carbon atoms have sp^3 hybridization,
- ➢ Four covalent bonds (σ-bonds),
- ➢ Insulators.



("File:Plastic Household Items.jpg" 2013)

❑ Conjugated polymers:

- ➢ Carbon atoms have sp^2 hybridization,
- ➢ Three covalent bonds (σ-bonds),
- ➢ Single free electron (p-Orbit),
- ➢ Semiconductors.



(plastics.tamu.edu)

("Conjugated Polymers" 2013)

Doped Polymers

- **Doping: redox reactions for the π electrons:**

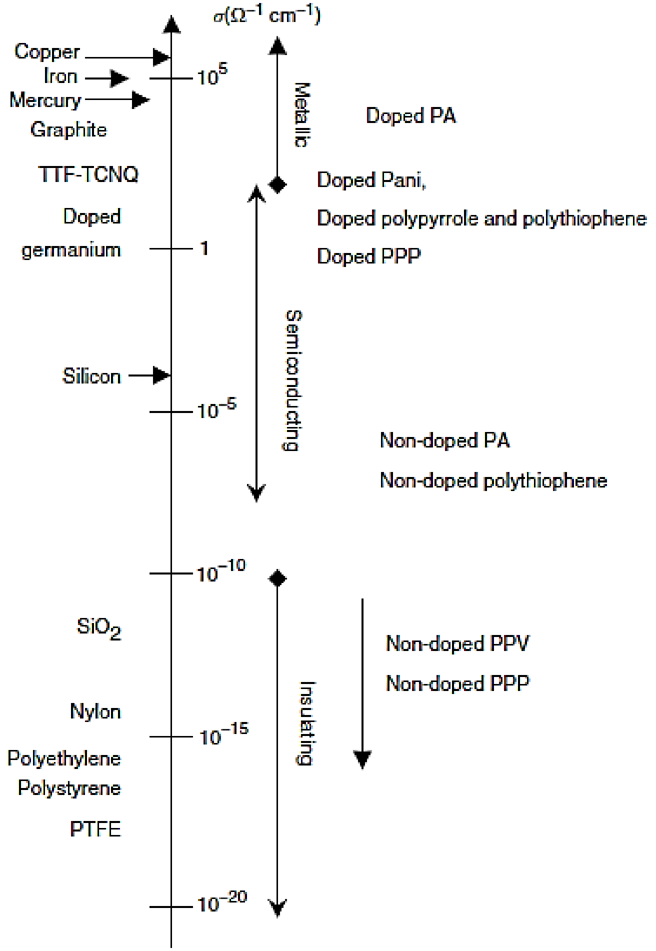
  Oxidation (p-doping)

  $$(Monomer)_n + \langle (xn)Anion^- \rangle \Rightarrow \left[(Monomer^{x+}) \langle (Anion^-)_x \rangle \right]_n + (xn)e^-$$

  Reduction (n-doping)

  $$(Monomer)_n + (xn)e^- + \langle (xn)Cation^+ \rangle \Rightarrow \left[(Monomer^{x-}) \langle (Cation^+)_x \rangle \right]_n$$

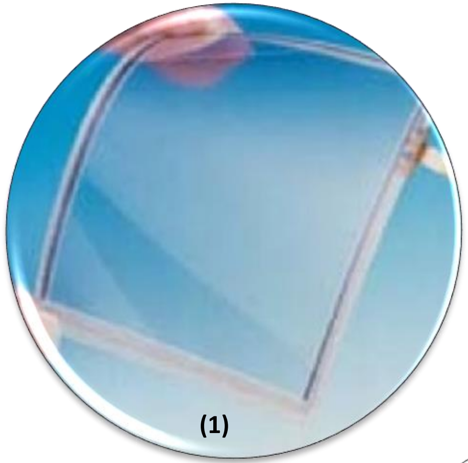
- **Offers a wide range of conductivity.**



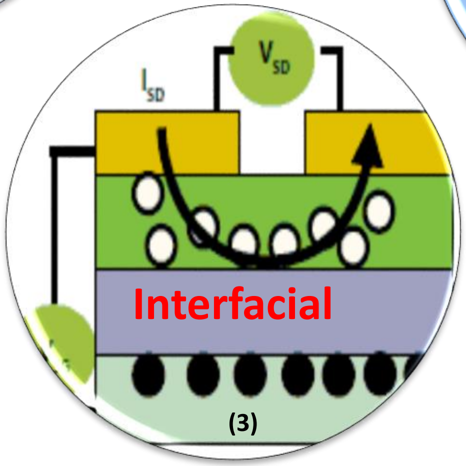
courtesy: Moliton and Hiorns 2004.

Doping in Conjugated Polymers

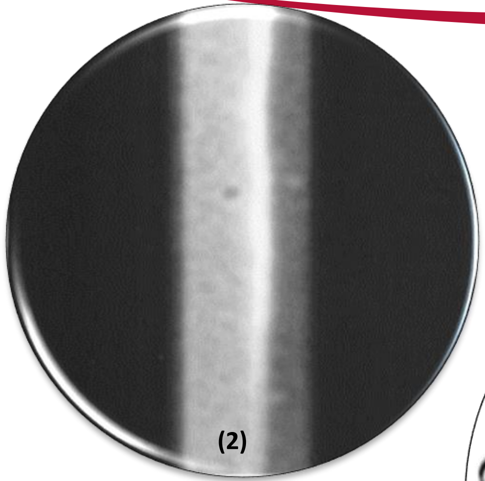
Doping in Conjugated Polymers



Chemical



Interfacial



Electro-chemical

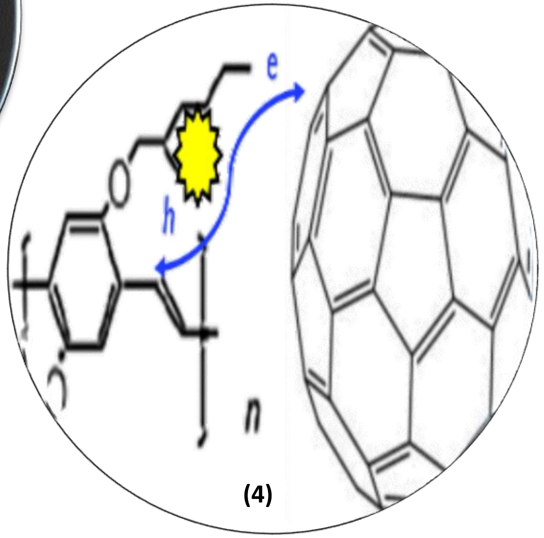
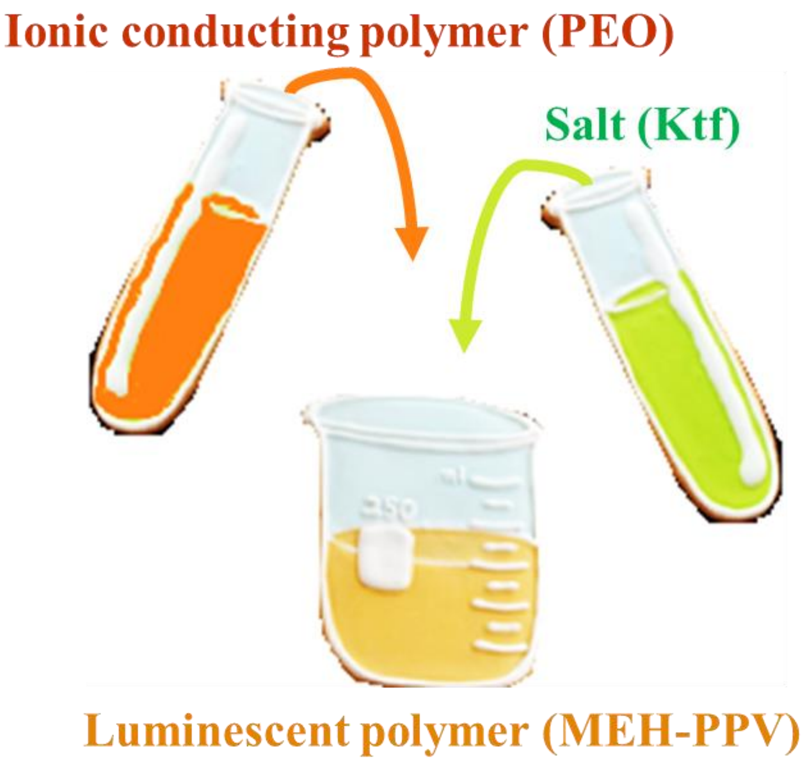


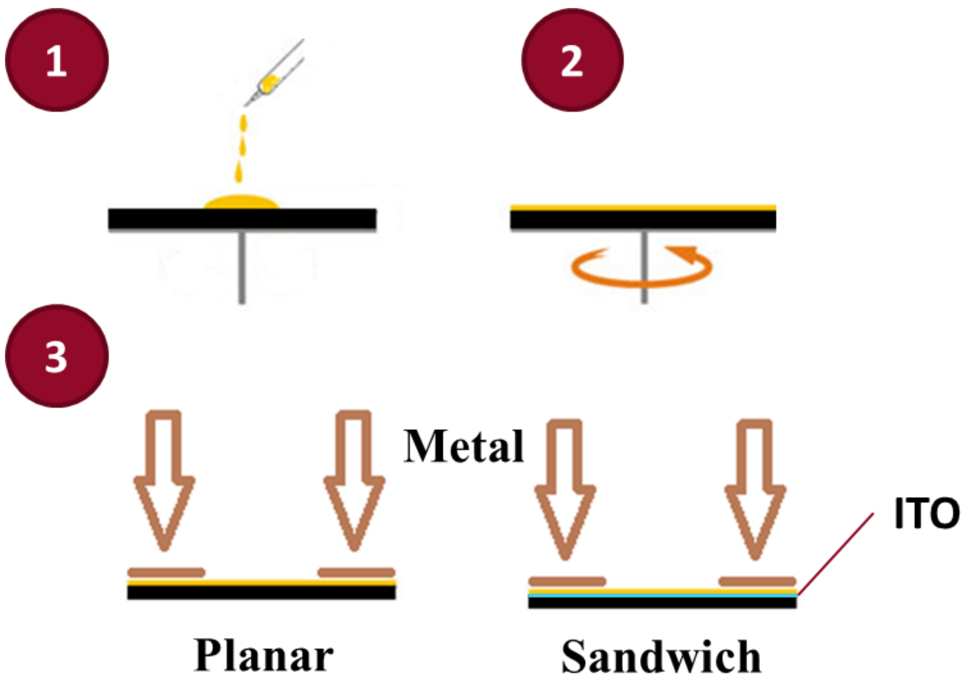
Photo-induced

Images courtesy:(1) http://miraimil.co.jp/pedotpss.html, (2) Pei, Qibing, et al., *Journal of the American Chemical Society* 118.16 (1996): 3922-3929.(4) http://www.sigmaaldrich.com/technical-documents/articles/material-matters/self-assembled-nanodielectrics.html

Polymer Light Emitting Electro-chemical Cells (PLECs)

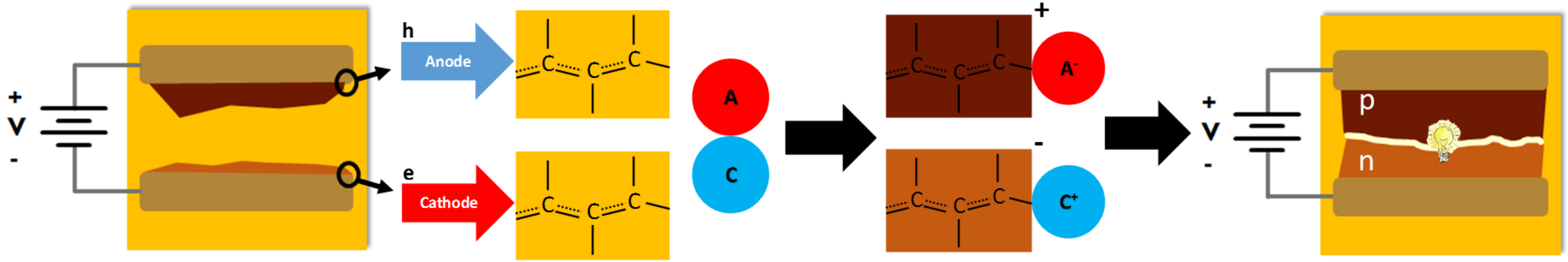
- ❑ Invented in 1995 by Qibing Pei and Alan Heeger,
- ❑ Blend of: luminescent polymer, ionic conducting polymer, and salt between two metallic electrodes.





PLEC Operation

- Principle: Electrochemical doping,
  - Oxidation and reduction reactions,
  - Doping propagation.



(**Faleh AlTal** and Jun Gao, "**Optical-Beam-Induced-Current Imaging of Planar Polymer Light-Emitting Electrochemical Cells**" in Light-Emitting Electrochemical Cells: Concepts, Advances and Challenges, Springer Nature, In press.)

Light Emitting Electro-chemical Cells (Pros/Cons)

Pros
❑ Reduced bulk resistance and electrode barriers,
❑ Operation independent of the electrodes materials,
❑ Low operation voltage can be achieved.
Cons
❑ Instability due to the dynamic junction nature,
❑ Large response time due to slow ionic transport.
Solution
❑ Fixed junction.

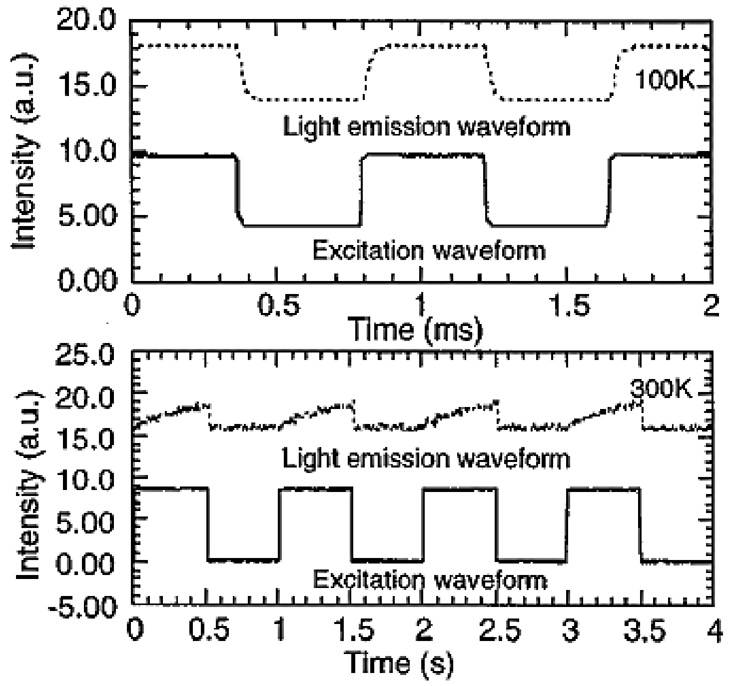
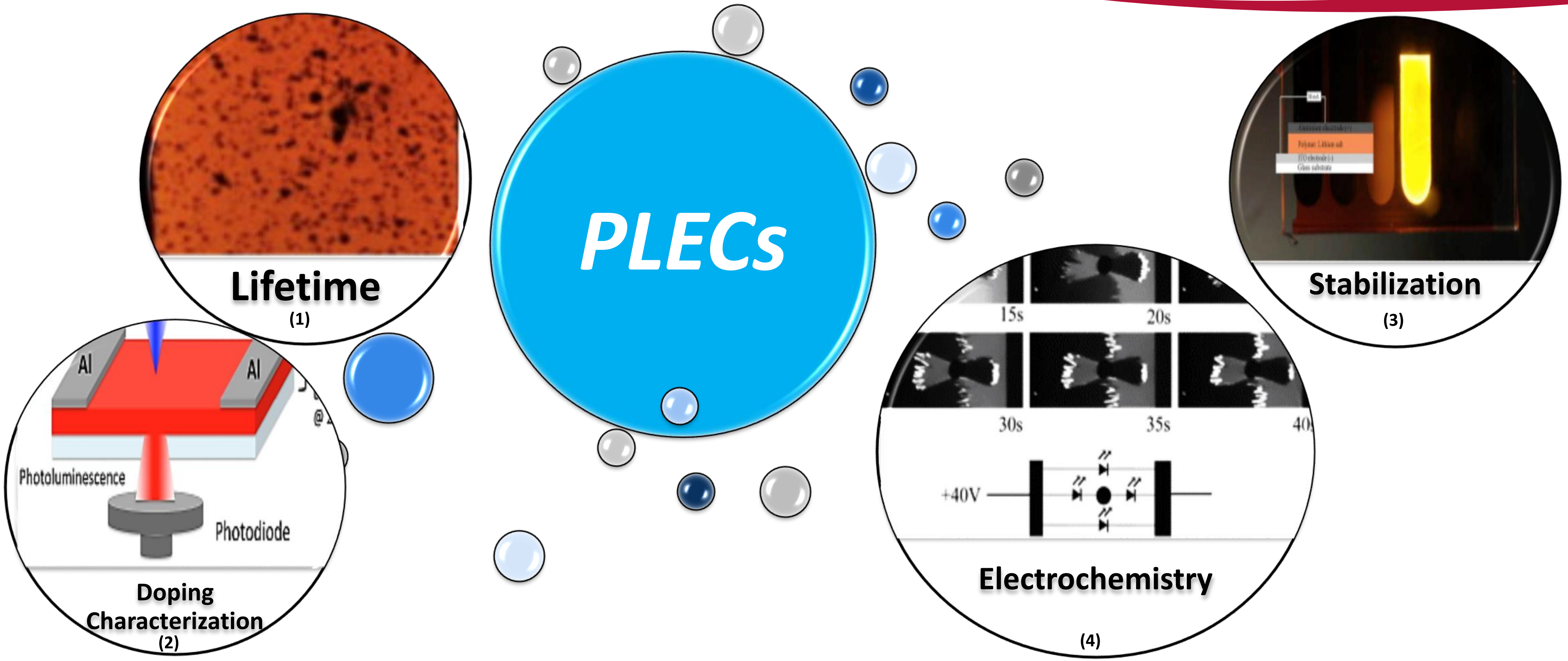


FIG. 2. Temporal response of the light emission of the frozen-junction LEC at 100 K (upper panel) and of the dynamic junction LEC at 300 K (lower panel).

J. Gao, G. Yu, and A. J. Heeger, *Applied Physics Letters*, vol. 71, no. 10, pp. 1293–1295, Sep. 1997.

PLEC Research (The Laboratory of Organic Photonics and Iontronics)

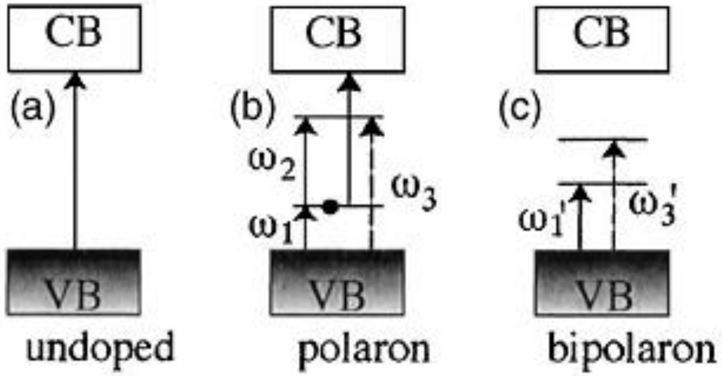


Images courtesy:(1) <u>**AlTal, F.**</u> & Gao, J., *Organic Electronics* **18,** 1–7 (2015), (2) Gautier, B., Wu, X., <u>**AlTal, F.**</u>, Chen, S. & Gao, J., *Organic Electronics* **28,** 47–52 (2016). (3) Chen, S., Wantz, G., Bouffier, L. & Gao, J.,. *ChemElectroChem* **3,** 392–398 (2016), (4) <u>**AlTal, F.**</u> & Gao, J., *Phys. Status Solidi RRL* **9,** 77–81 (2015).

Doping-induced Luminescence Quenching

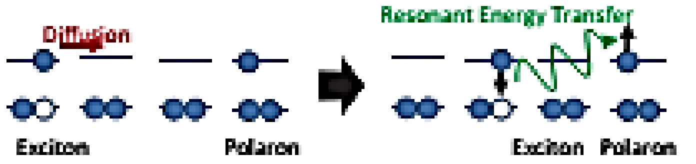
$$S_{if} = \frac{2m\omega_{if}}{\hbar} |\langle Q_i | x | Q_f \rangle|^2,$$

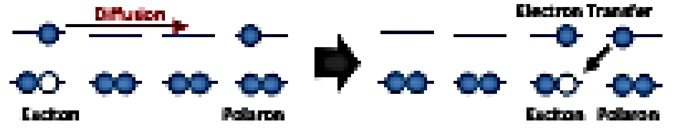
$$\sum_{i>j} S_{ji} = 1$$

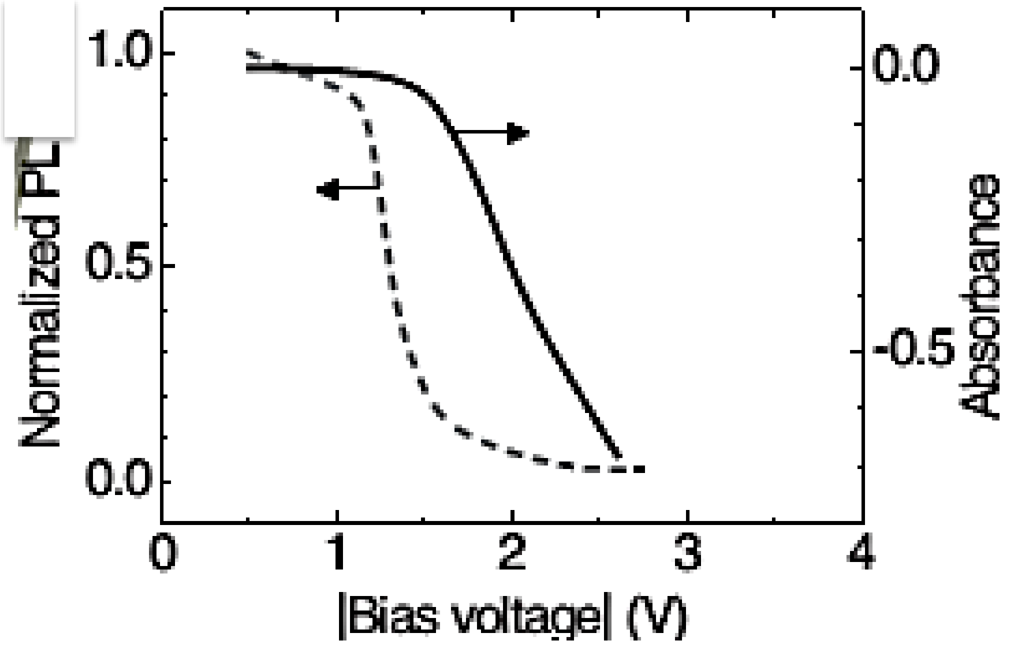


A. L. Holt, J. M. Leger, and S. A. Carter, *The Journal of Chemical Physics*, vol. 123, no. 4, p. 44704, Jul. 2005.

Förster resonance energy transfer	Charge transfer



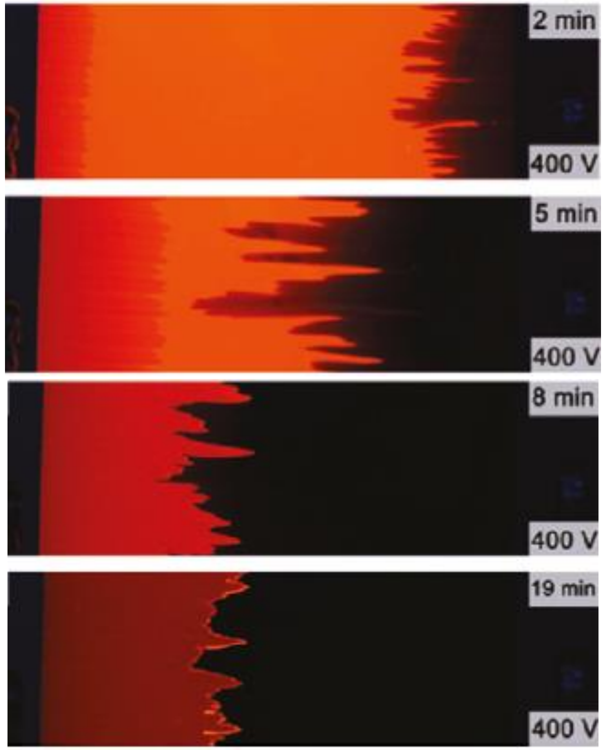




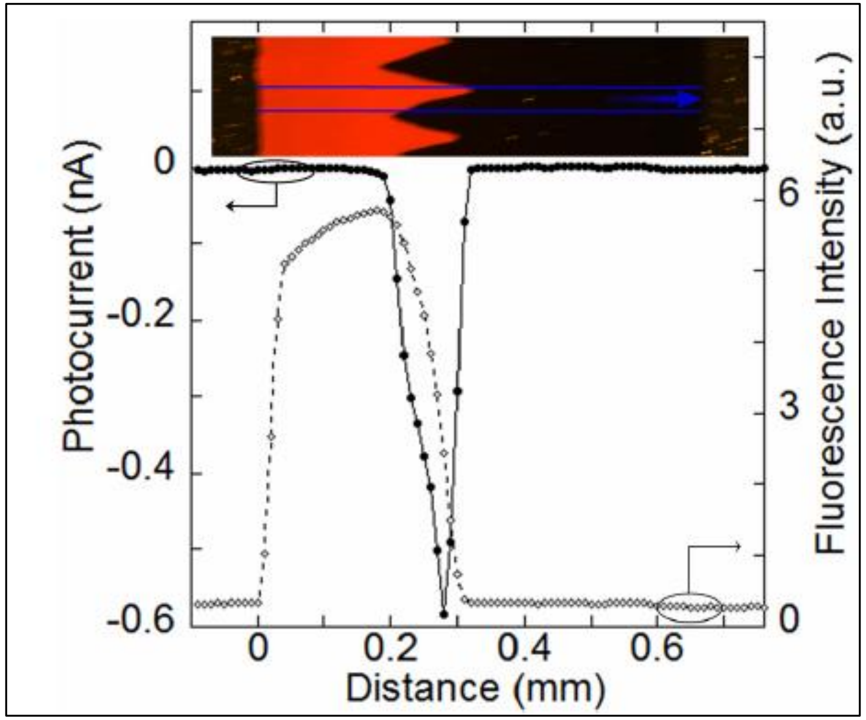
S. van Reenen, M. V. Vitorino, S. C. J. Meskers, R. A. J. Janssen, and M. Kemerink, *Phys. Rev. B*, vol. 89, no. 20, p. 205206, May 2014.

Electrochemical Doping in PLECs

- Electrochemical doping was observed as luminescence quenching,
- Experiments showed evidence for junction field.



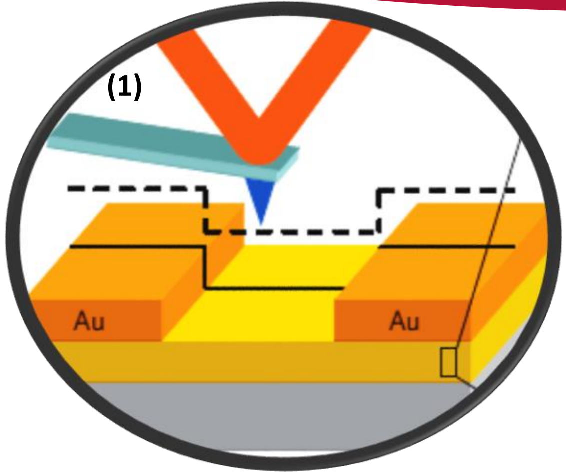
(Hu Y, Gao J. J Am Chem Soc. 2011)



(Inayeh A, Dorin B, Gao J.. Applied Physics Letters. 2012)

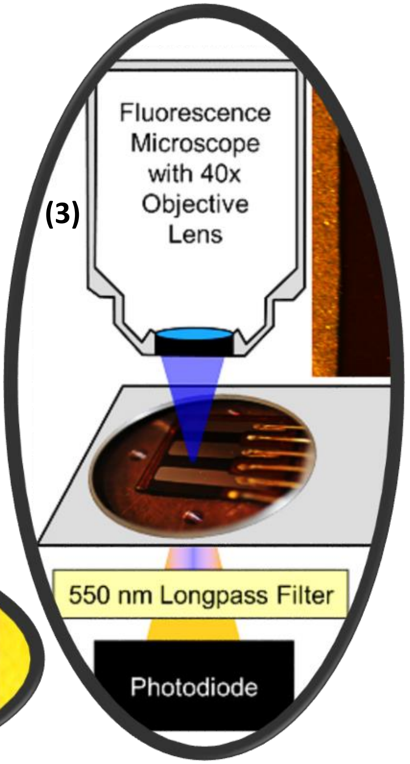
Scanning Measurements for PLEC

- ❑ **Goal: Resolving the p-n junction field of PLECs.**
- ❑ **Unfrozen devices:**
  - ➢ Some measurements were done under bias.
  - ➢ At no bias the devices were prone to relaxation.
- ❑ **Frozen devices:**
  - ➢ The used probes and step size were very large.



Scanning Kelvin Probe

Micro manipulated probes



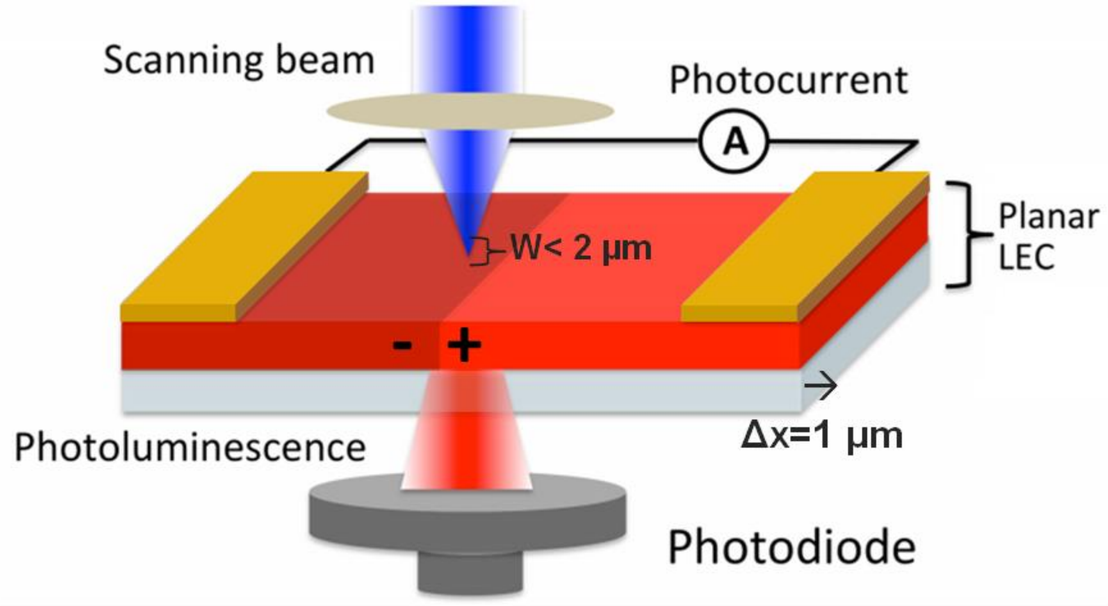
OBIC and PL Scanning

(1) P. Matyba, K. Maturova, M. Kemerink, N. D. Robinson, and L. Edman, *Nat Mater*, vol. 8, no. 8, pp. 672–676, Aug. 2009.
(2) Y. Hu and J. Gao, *J. Am. Chem. Soc.*, vol. 133, no. 7, pp. 2227–2231, Feb. 2011.
(3) A. Inayeh, B. Dorin, and J. Gao, *Applied Physics Letters*, vol. 101, no. 25, p. 253305, Dec. 2012.

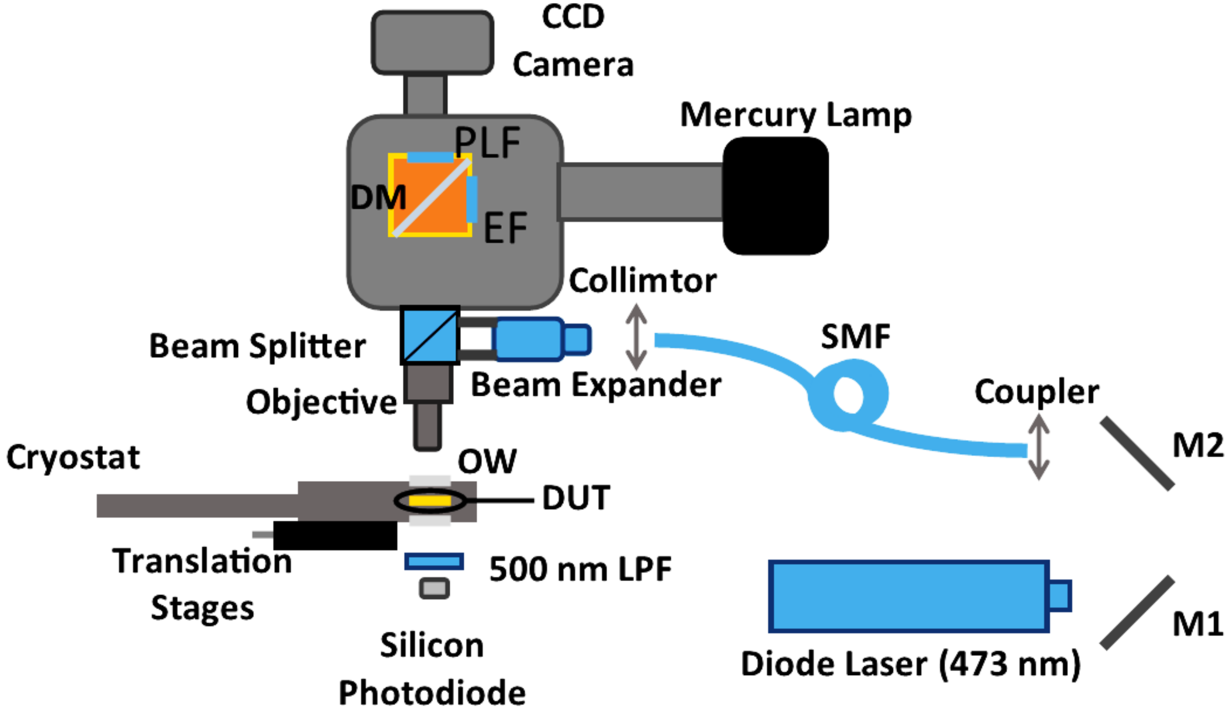
Optical Beam Induced current (OBIC) and Photoluminescence (PL) Scanning Setup

❑ **Short circuit photo-current is generated at regions with built in electric field.**

(Faleh AlTal and Jun Gao, "**Optical-Beam-Induced-Current Imaging of Planar Polymer Light-Emitting Electrochemical Cells**" in Light-Emitting Electrochemical Cells: Concepts, Advances and Challenges, Springer Nature, In press.)

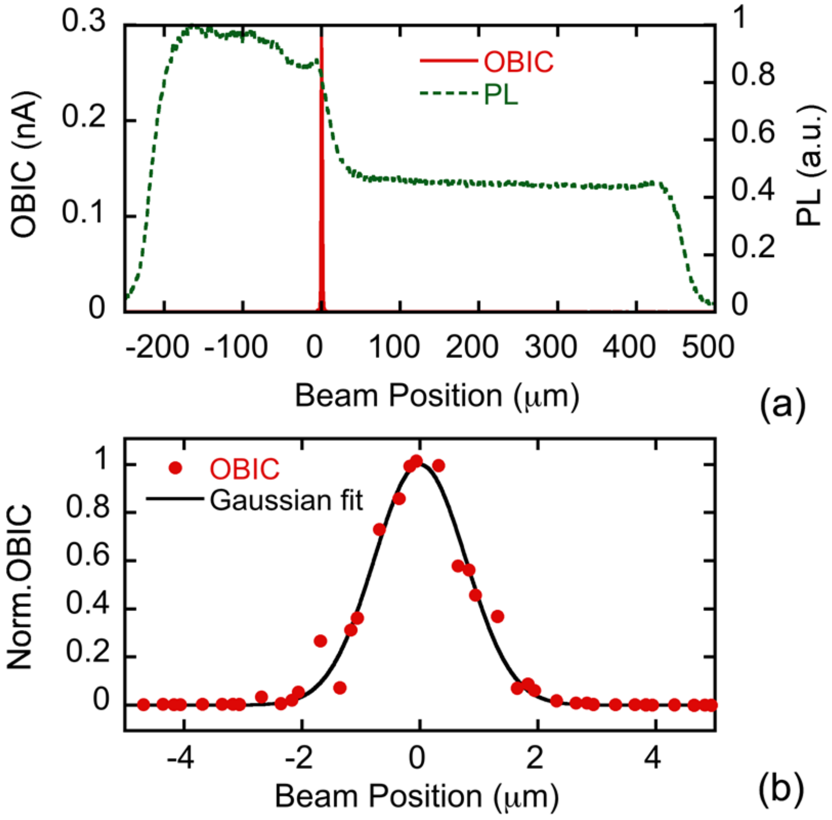


Adapted from: **F. AlTal**, J. Gao, Phys. Status Solidi Rapid Res. Lett. **9**, 77–81 (2015)

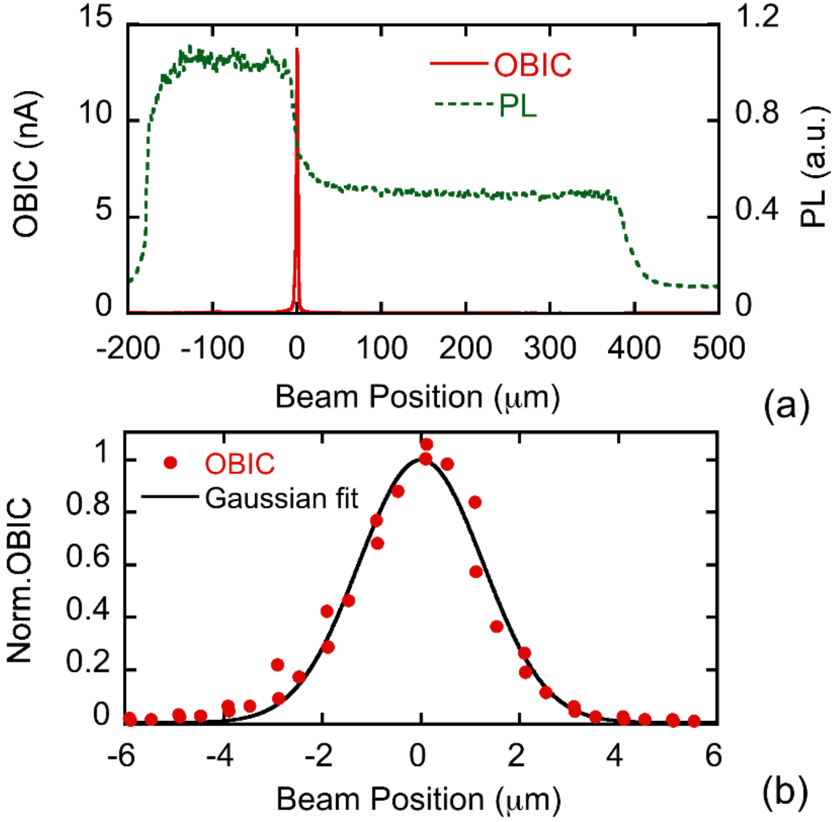


F. AlTal, J. Gao, J. Appl. Phys. **120**, 8 (2016)

OBIC/PL Profiles of PLECs



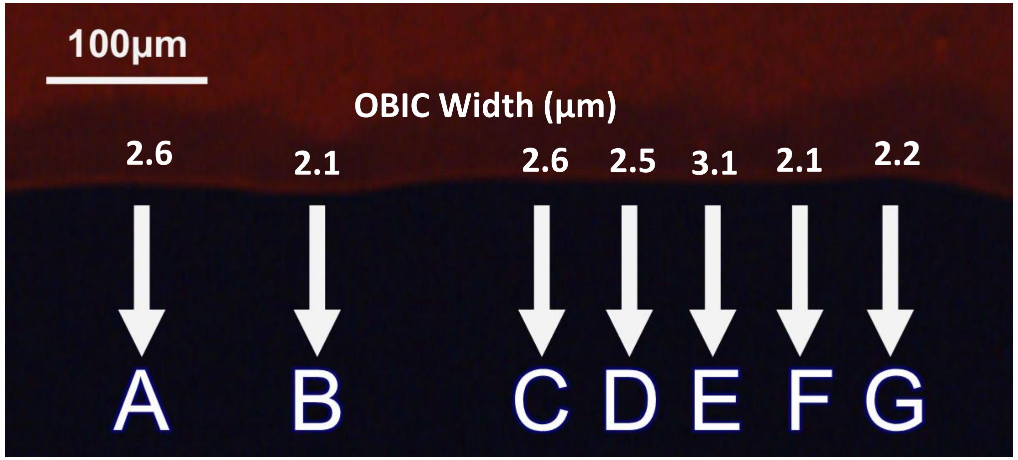
F. AlTal, J. Gao, J. Appl. Phys. **120**, 8 (2016)

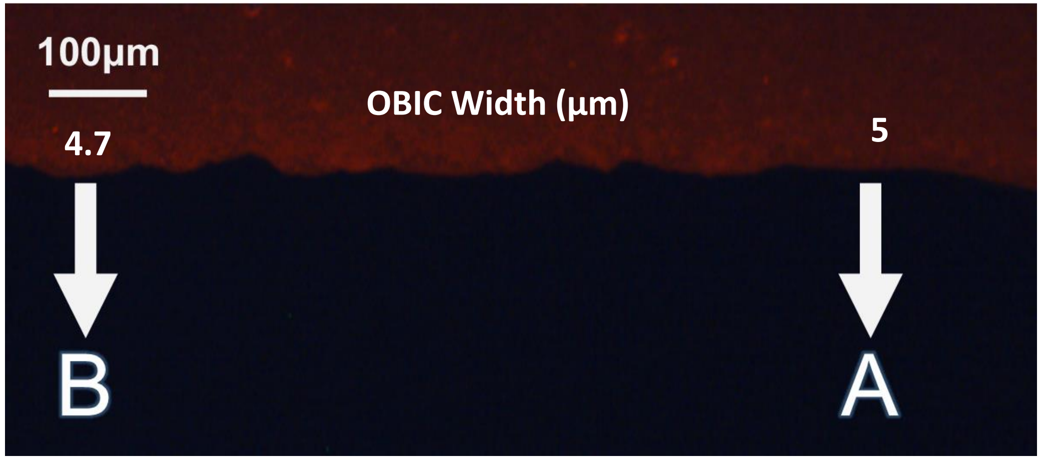


F. AlTal and J. Gao, *Sci. China Chem.*, vol. 60, no. 4, pp. 497–503, Apr. 2017.

OBIC Profiles of PLECs

- ❑ The resolved average depletion widths accounted for a portion of the total cell width as small as 0.2 % (1.5 µm):
  - ➢ **The smallest so far, as proportion and absolute width.**





F. AlTal, J. Gao, J. Appl. Phys. **120**, 8 (2016)

F. AlTal and J. Gao, *Sci. China Chem.*, vol. 60, no. 4, pp. 497–503, Apr. 2017.

PLEC OBIC Profiles Calculations

- Drift-diffusion

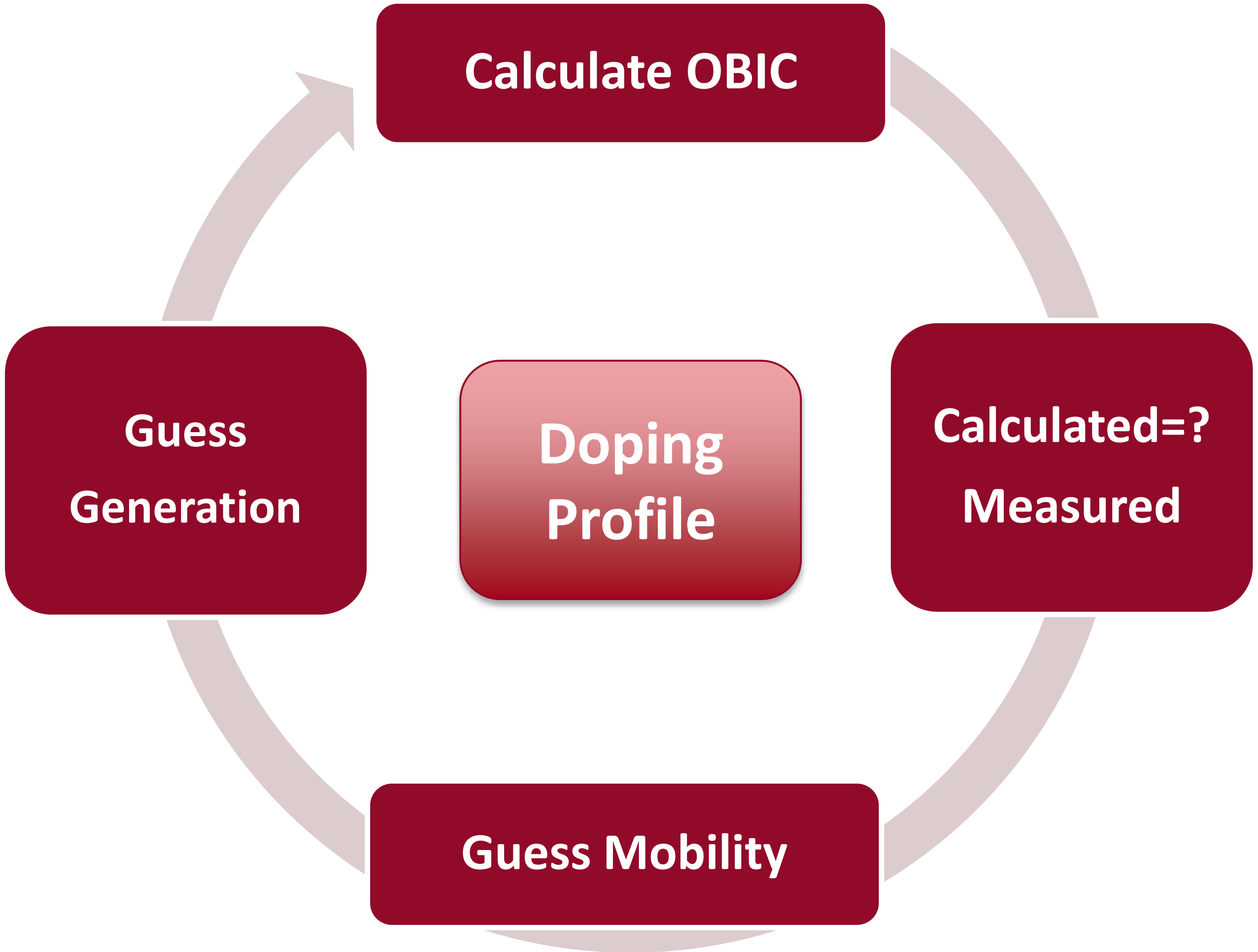
$$J_e = qD_e \nabla n - q\mu_e n \nabla u$$

$$J_h = -qD_h \nabla p - q\mu_h p \nabla u$$

- Continuity

$$\nabla . J_e + q(G - Q(np - n_i^2)) = 0$$

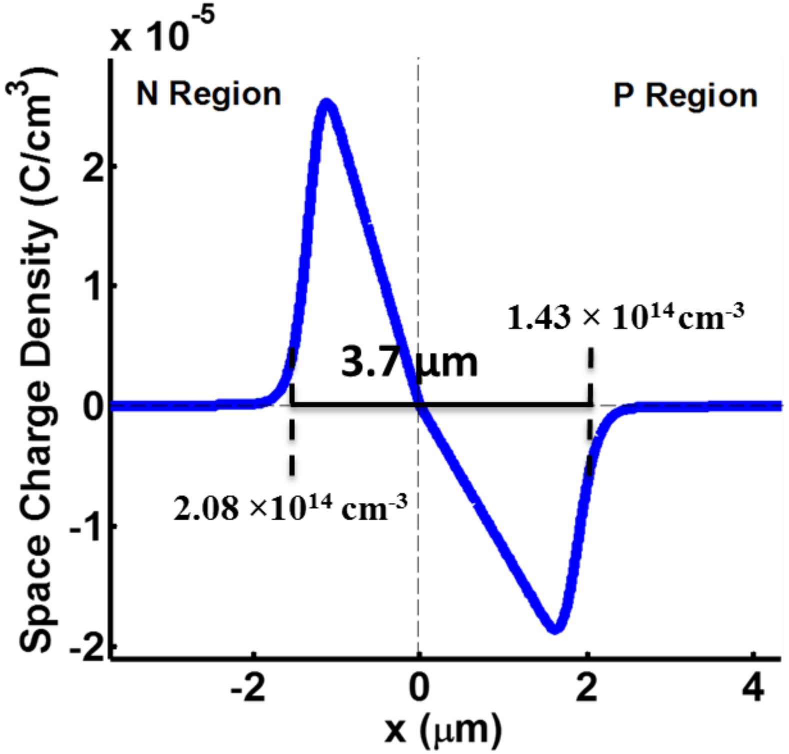
$$-\nabla . J_h + q(G - Q(np - n_i^2)) = 0$$



PLEC Depletion Region/Doping Profile

- The junction doping level was determined using drift diffusion calculations ($10^{14} \sim 10^{15}$ cm^{-3}).

SC density reproducing the 4.7 µm OBIC signal



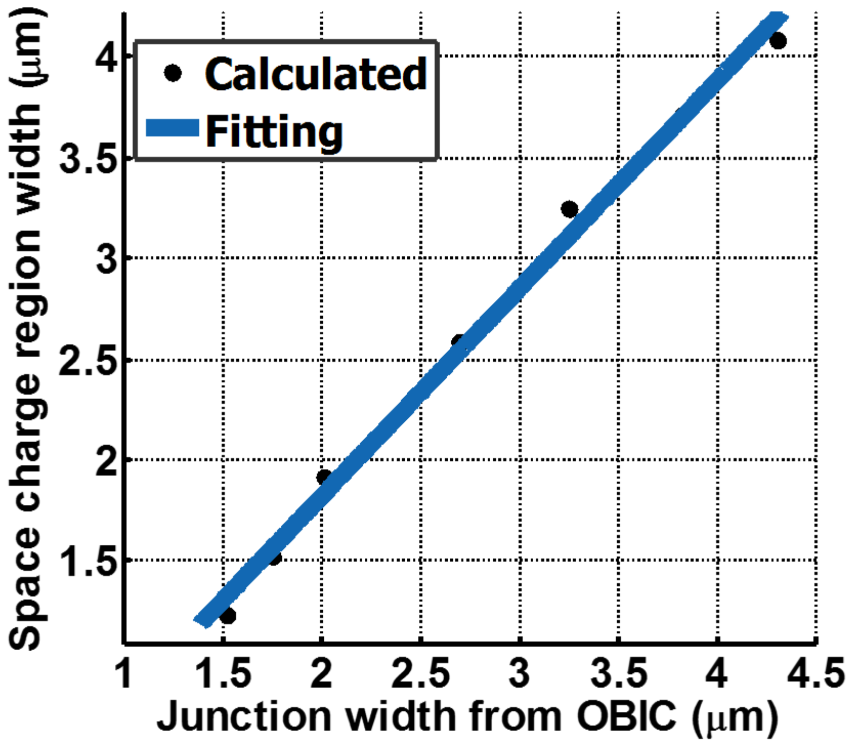
AlTal, Faleh, and Gao, Jun, *Science China Chemistry* 60.4 (2017): 497-503.

OBIC: Drift-Diffusion Calculations

Queen's University

- ❑ Does deconvolution of Gaussians ($W_d = \sqrt{W_{OBIC}^2 - W_{Beam}^2}$) gives a good estimate for the depletion width ?
- ❑ Matching the measured to the calculated OBIC profile:
- ➢ Mobility 160~600 cm^{2}/(V.s), orders of magnitude larger than reported for sandwich un-doped devices.
- ➢ Photon to free carrier conversion of ~ 1% was determined.

  ➔ Consistent with the measured values in literature.



$\left(\sqrt{W_{OBIC}^2 - W_{Beam}^2}\right)$

Faleh Altal., 2017. (Doctoral dissertation).

Conclusion

- PLECs provide a platform for diverse research avenues,
- The resolved junction in a planar PLEC was as small as 0.2% of the cell volume,
- Deconvolution the beam profile from the OBIC profile provides a good estimate for the depletion width,
- Polymer characteristic parameters were determined by comparing the measured OBIC profiles to the calculated profiles.

Questions

Thank You

Acknowledgements
The optical scanning studies were supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).
Faleh AlTal was supported by an Ontario Trillium Fellowship provided by the government of Ontario.