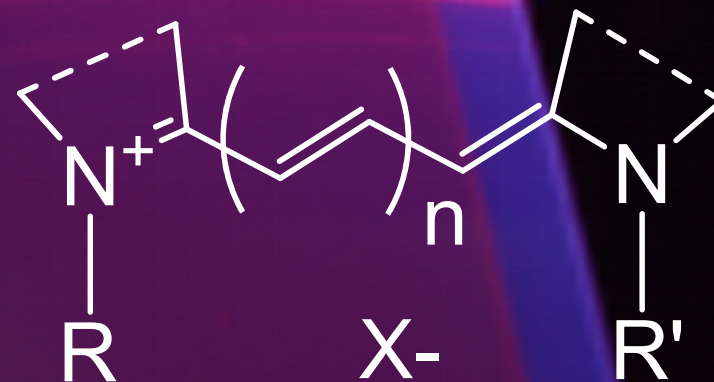


(Novel Organic Material for PV Applications)

Solution-Processable, Small Molecules for All-Organic Solar Cells

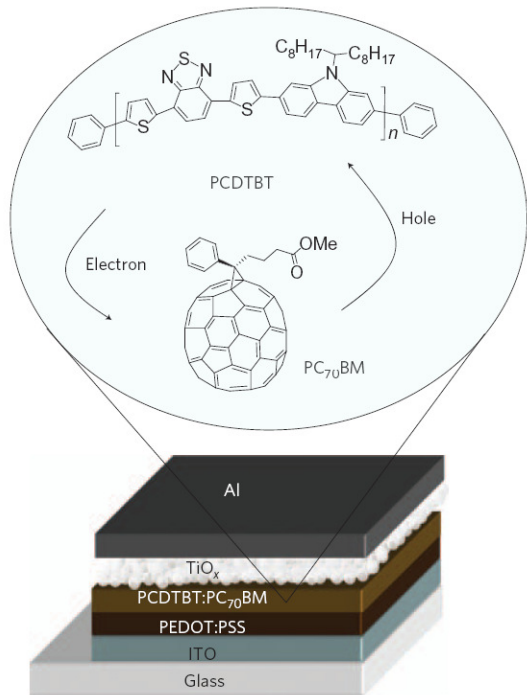
Roland Hany

*Empa – Laboratory for
Functional Polymers
CH-8600 Dübendorf*

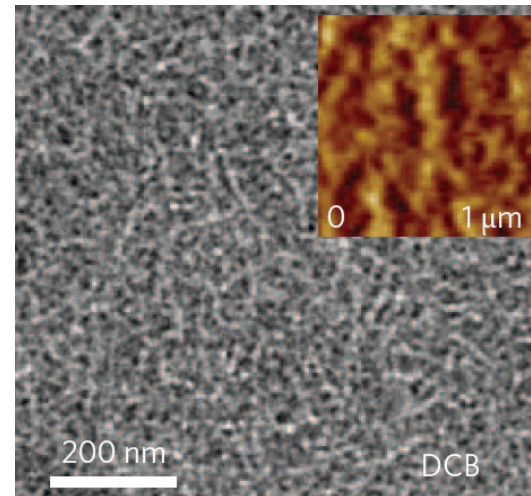


Materials Science & Technology

State-of-the-Art: Polymer-PCBM Bulk OPV

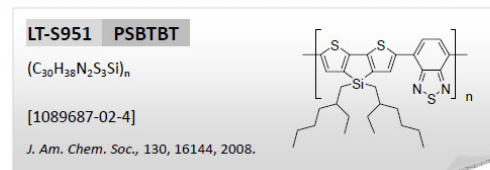
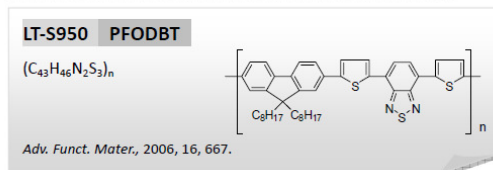
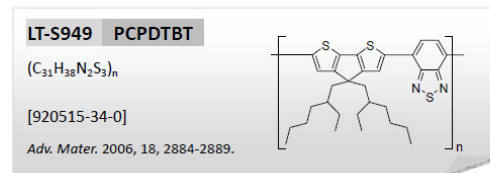
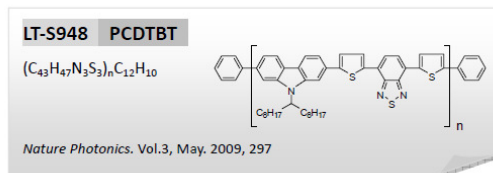


$\eta = 6\%$



A. J. Heeger et al., *Nature Photonics*, **3**, 297 (2009)

Advanced Low Bandgap Polymer Materials



Morphology

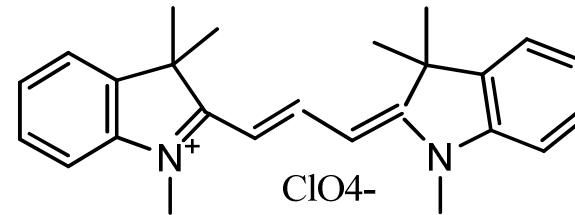
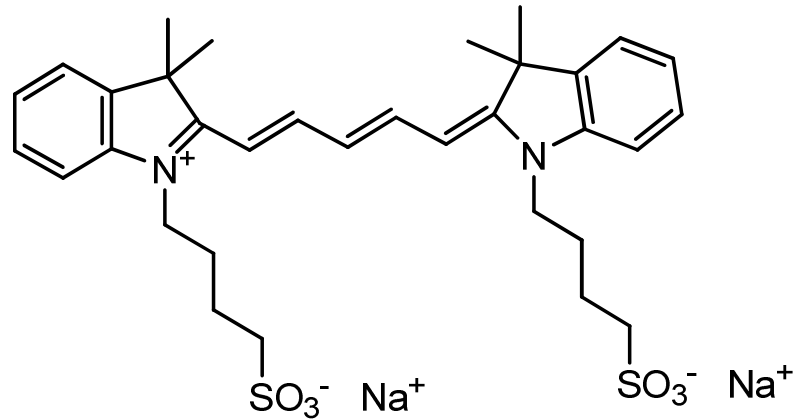
Polymer
Synthesis

OPV with solution-processable small molecules

Small molecules tend to crystallize – poor film formation

| | | |
|--|--------------------|---------------|
| Review Materialstoday 10(11), 2007, 34 | $\eta(\text{max})$ | = 1.3% |
| Chem. Commun. 2008, 6489 | | = 1.7% |
| JACS 2008, 130, 17640 | | = 1.2% |
| Org. Electronics 2008, 9, 85 | | = 1.2% (Empa) |
| Chem. Mater. 2009, 21, 1413 | | = 1.5% |
| Int. J. Photoenergy 2009, in press | | = 1.0% (Empa) |
| Adv. Mater 2009, submitted | | = 2.6% (Empa) |

Cyanine Dyes



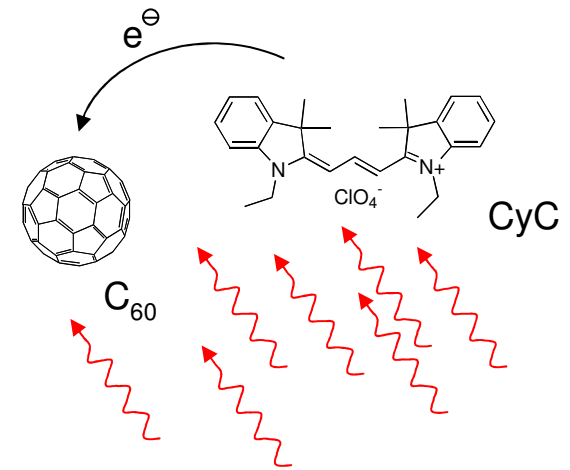
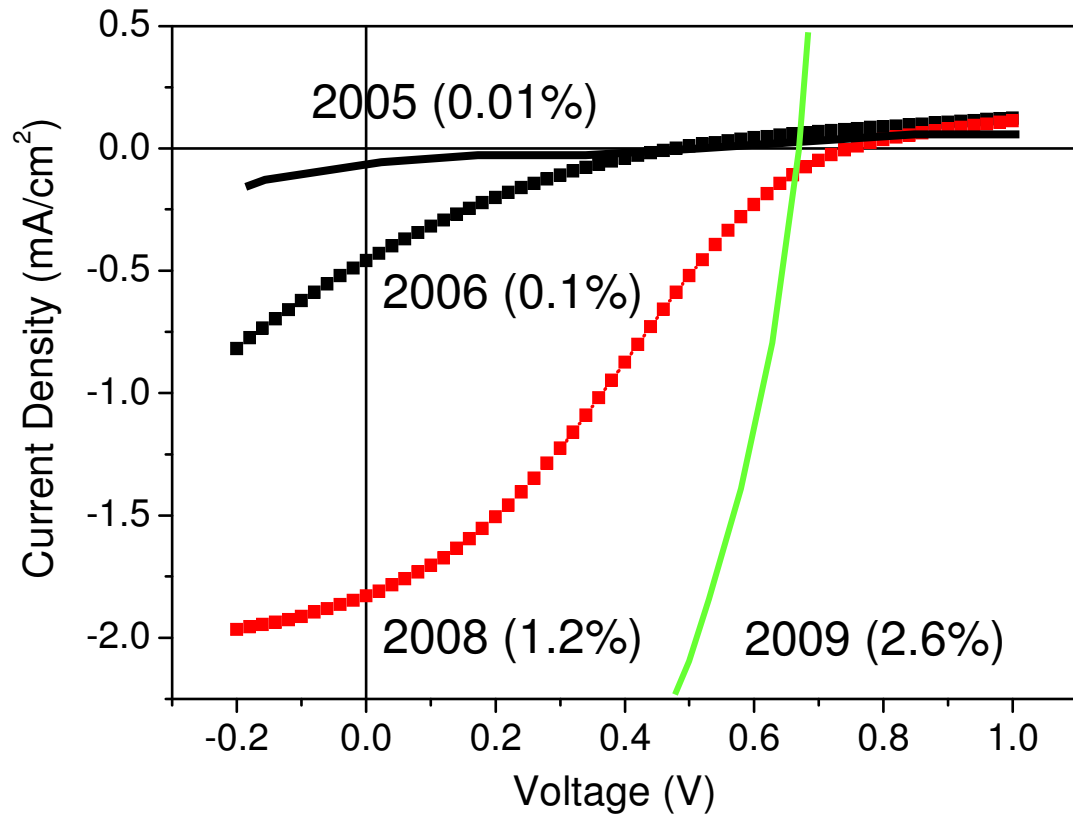
Very high extinction coefficient

Tunable absorption from the UV to the NIR

Processable in many organic solvents, good film-forming properties

Commercial available, “simple” synthesis and purification

Towards high performance bilayer cyanine OSC



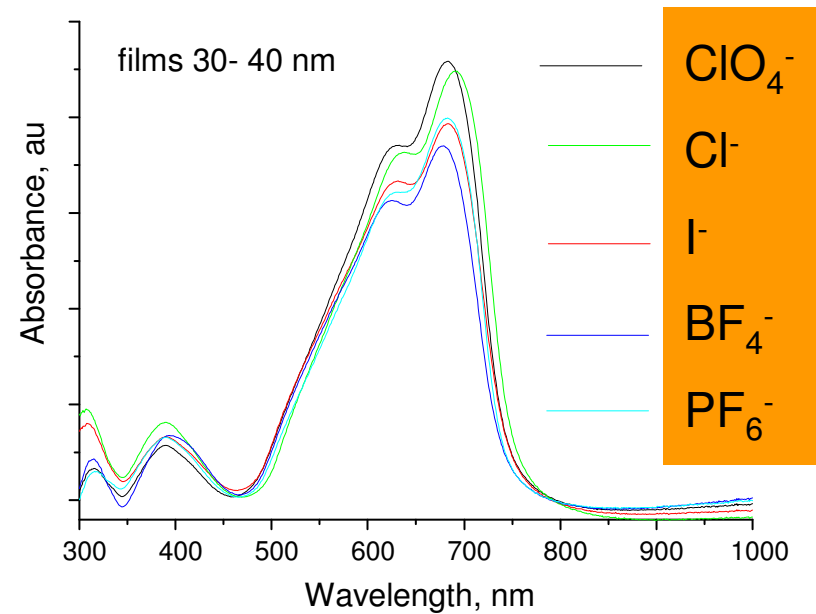
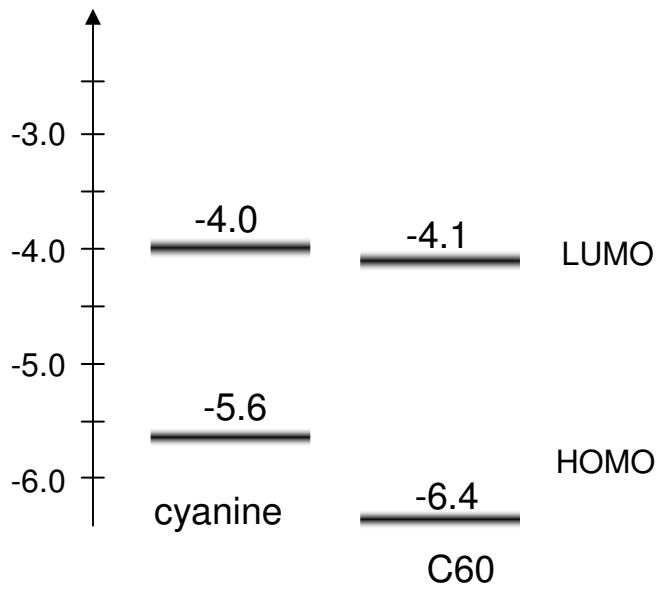
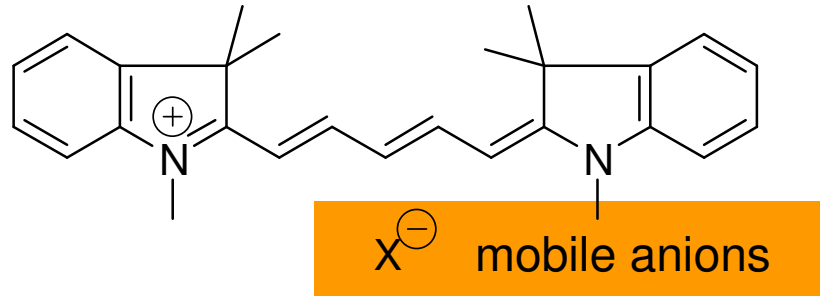
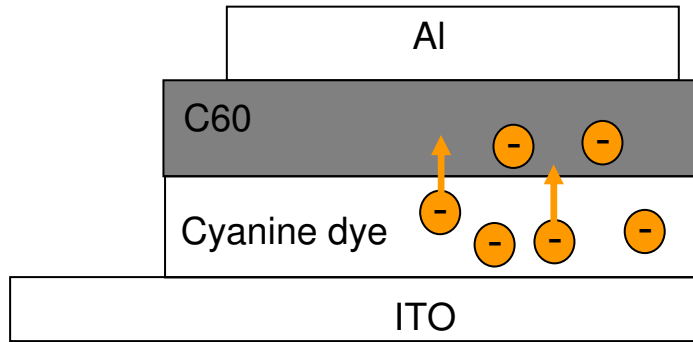
- ◆ - Undoped

- ◆ - Doped with O₂, light and water

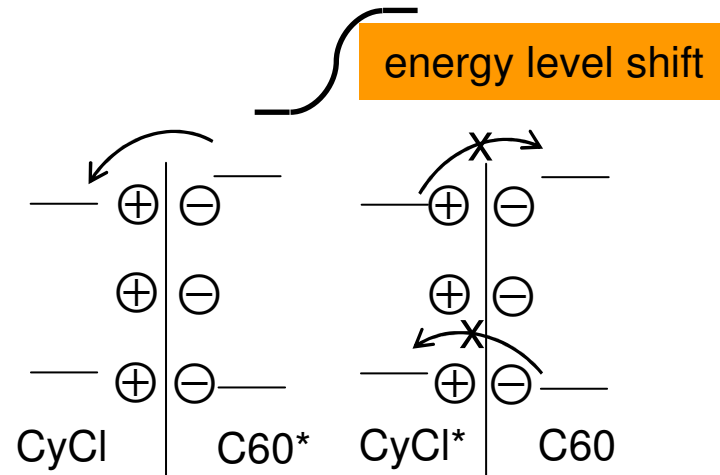
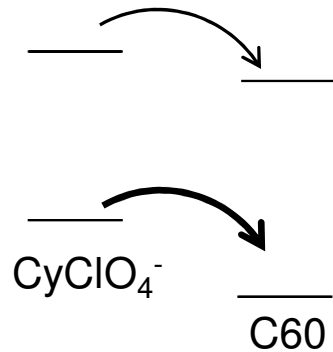
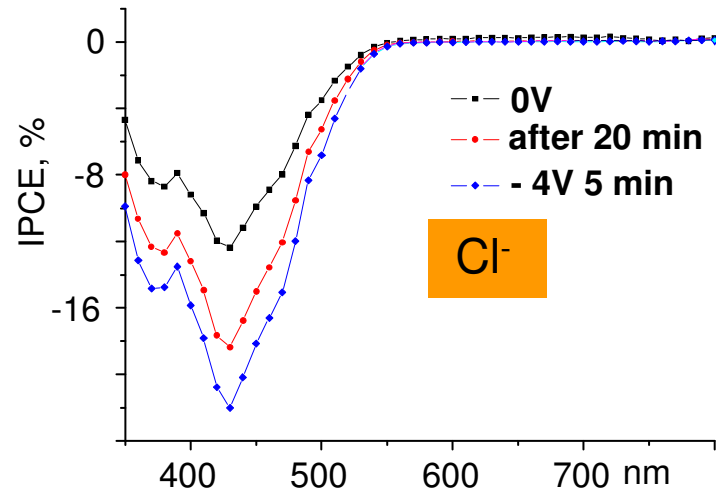
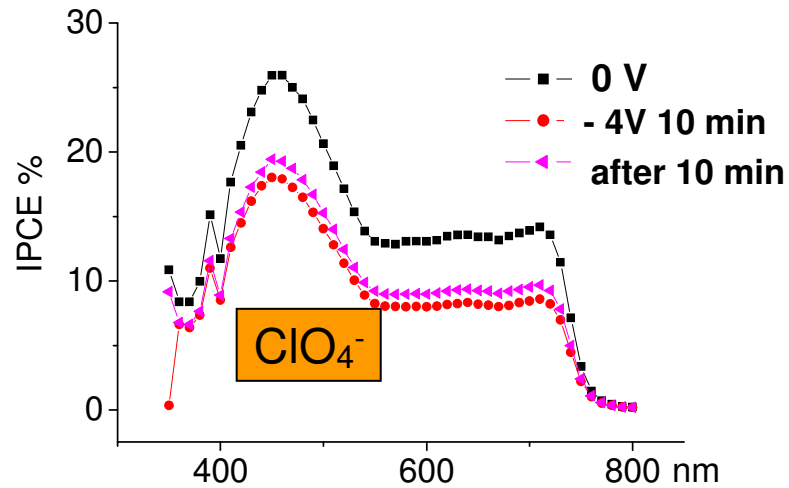
- ◆ - Doped with NO⁺BF₄⁻

Latest news: $\eta = (3.5 - 4.5)\%$

Ionic space charge driven devices



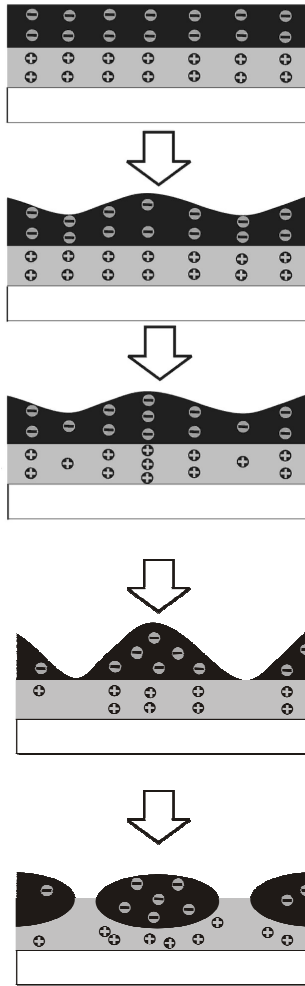
Ionic charge controls flow of electronic current



Chimia 2007, 61, 787

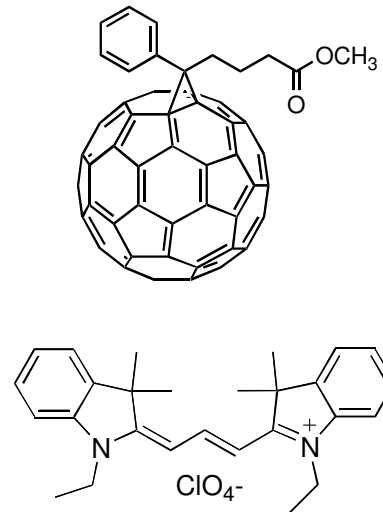
PCCP, 2009, DOI:10.1039/B909512H

Liquid-liquid dewetting in evaporating Cyanine dye – PCBM film



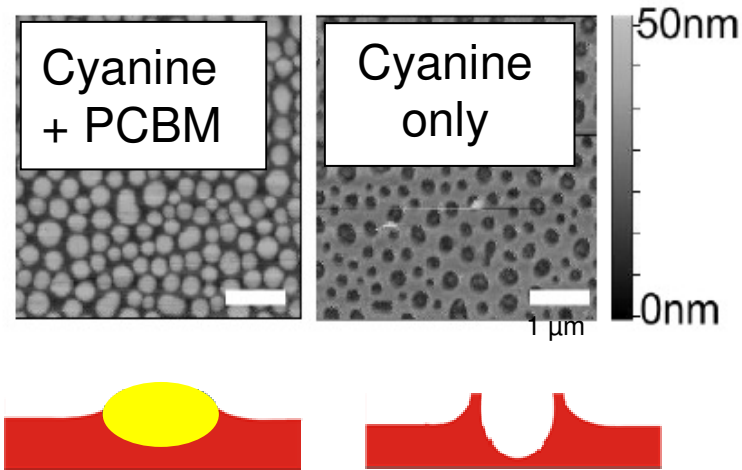
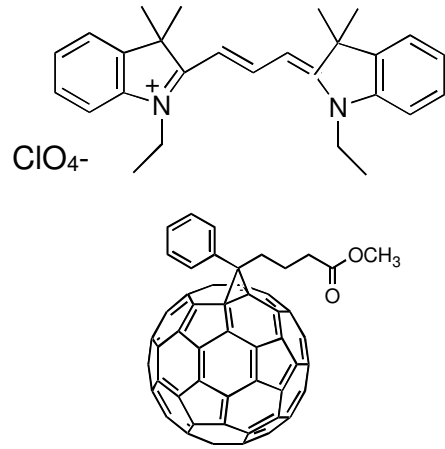
Transient bilayer

Electrostatic disjoining pressure - Fluctuations are amplified
– Spinodal dewetting



Charged
domains

Liquid-liquid dewetting: Tuning of morphology



Parameters

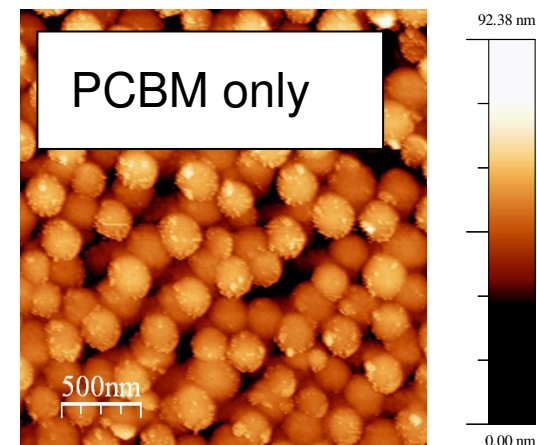
Counter Anion

Cyanine Dye

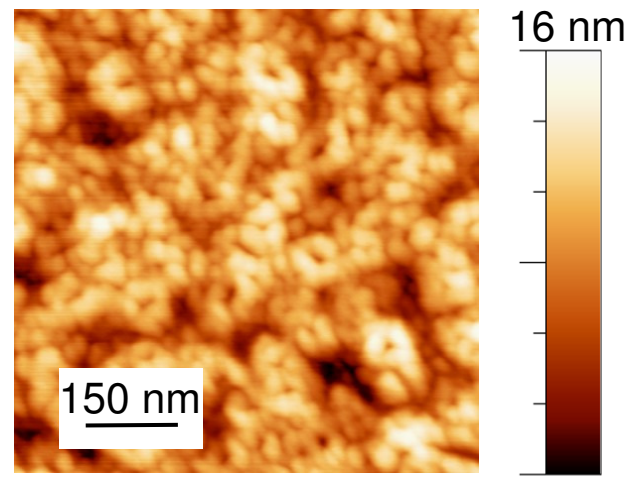
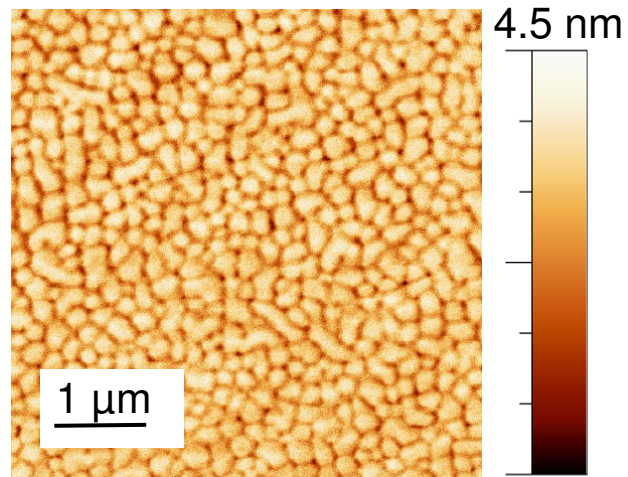
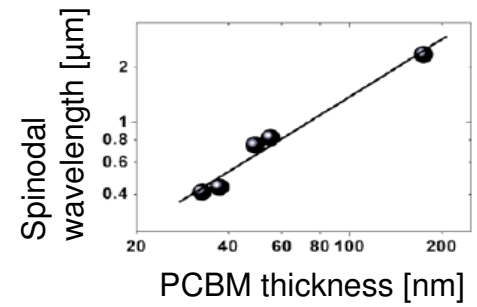
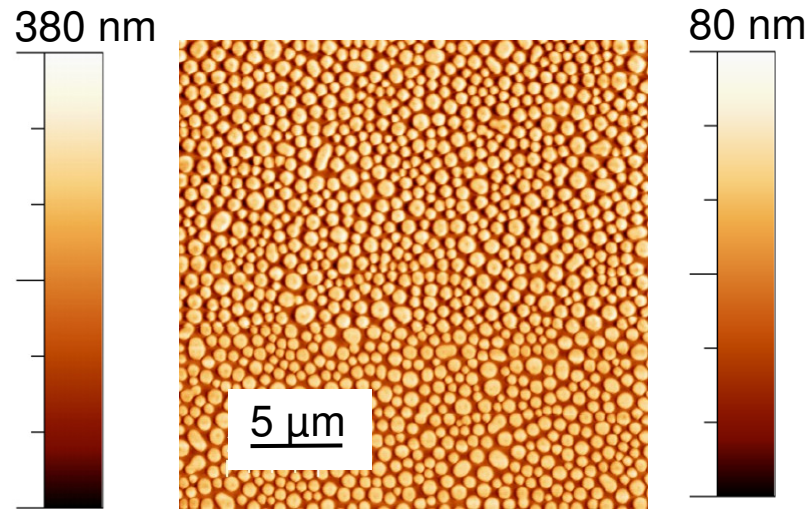
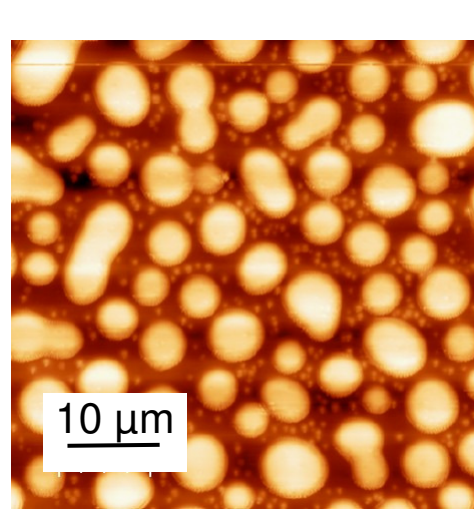
[PCBM] / [Cyanine]

Solvent

Temperature...

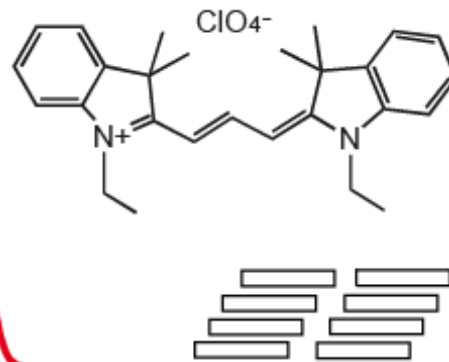
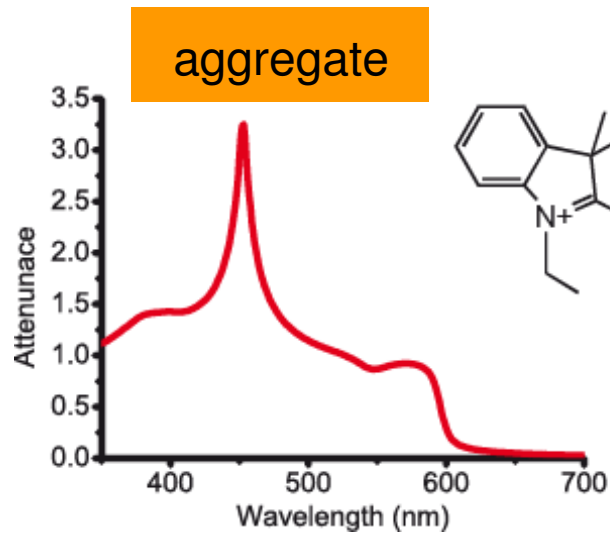
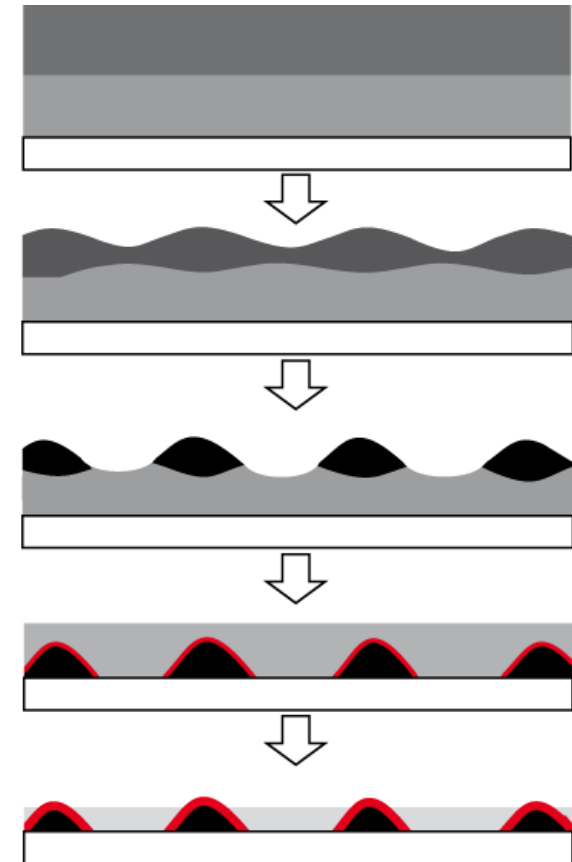
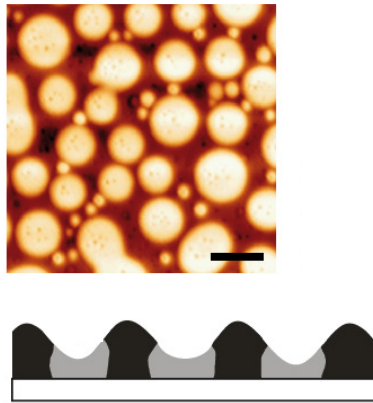
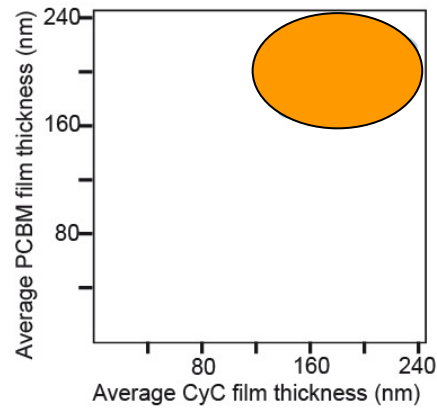


Liquid-liquid dewetting: Tuning of morphology

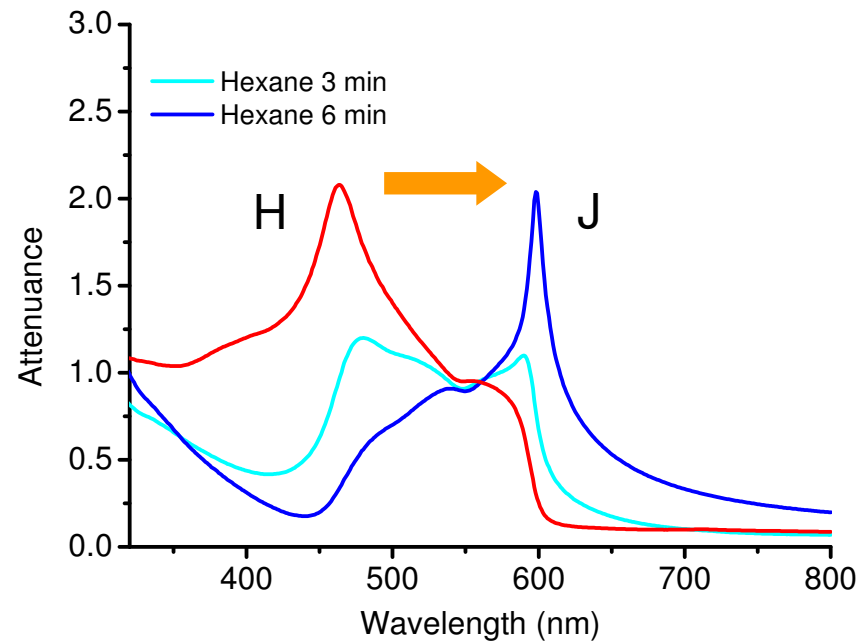
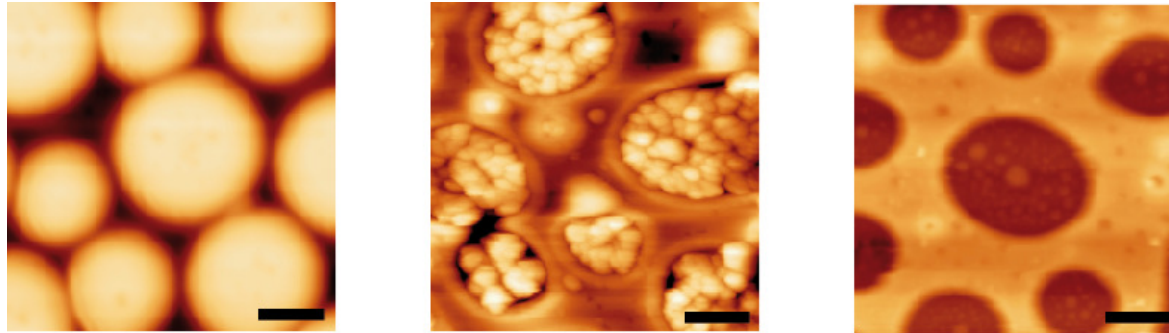


Work in progress:
Bulk cyanine-
PCBM solar cells
with *known*
morphology

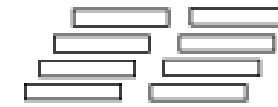
Cyanine Aggregates via Liquid-Liquid Dewetting



Cyanine Aggregates via Liquid-Liquid Dewetting



H-aggregate



J-Aggregate

Cyanine Aggregates via Liquid-Liquid Dewetting

Merits

Aggregation from aprotic, apolar solvents

Aggregation is very, very fast

H- and J-aggregates of high quality

Patent www.switt.ch

„J-aggregates of cyanine dyes by self-assembly“, R. Steiger et al, Colloid & Interfaces B, December 2009

Work in progress

Light-harvesting and charge-transporting aggregates in OSC.

Conclusions

High cyanine *extinction coefficients* allow to use thin absorbing films in *bilayer* organic solar cell architecture

Small soluble molecules achieve *high efficiency* in organic solar cell devices

Cyanines are produced on large scales, are cheap and easy to purify

Mobile Cy^+X^- anions offer advanced device functionalities, such as control of flow of electronic current, submicron patterning of blend films or aggregate formation from organic solvent

Acknowledgement

Jakob Heier

Hadjar Benmansour

Fernando Castro

Fan Bin

Ylenia Maniglio

William Kylberg

Frank Nüesch

Rolf Steiger

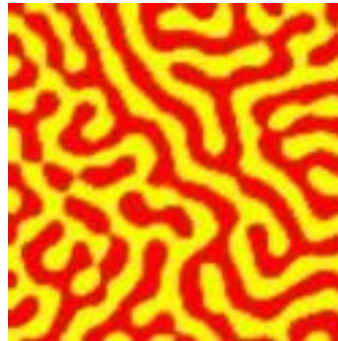
Tom Mates



Structure formation in evaporating blend film – driving forces

solvent vapor pressure –
kinetically trapped
structures

surface energies – wetting
/ dewetting

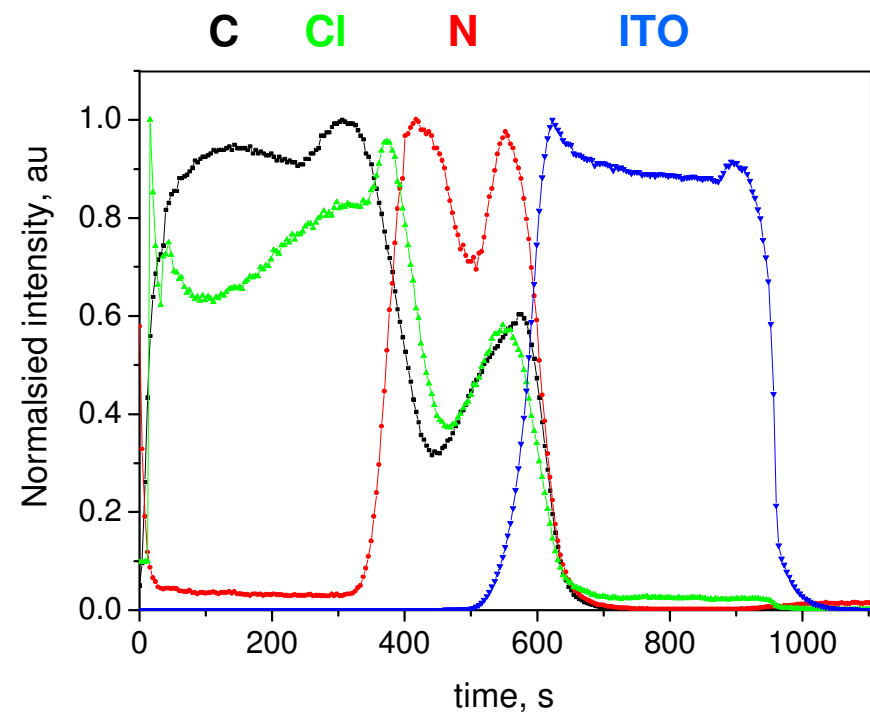
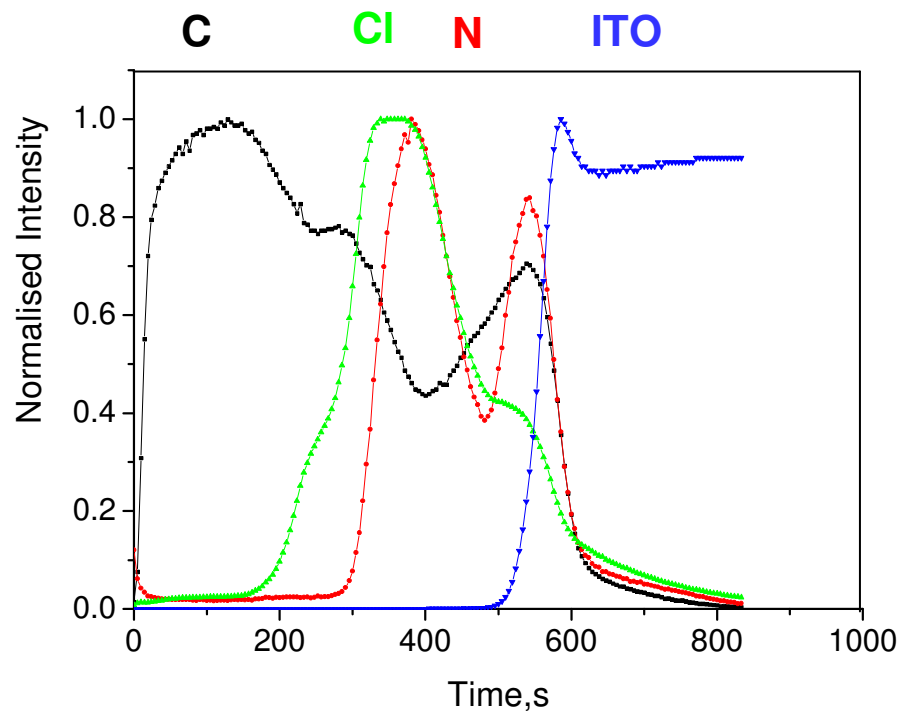
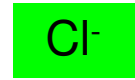
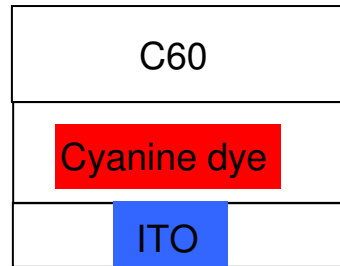


interaction parameters –
polymer phase separation

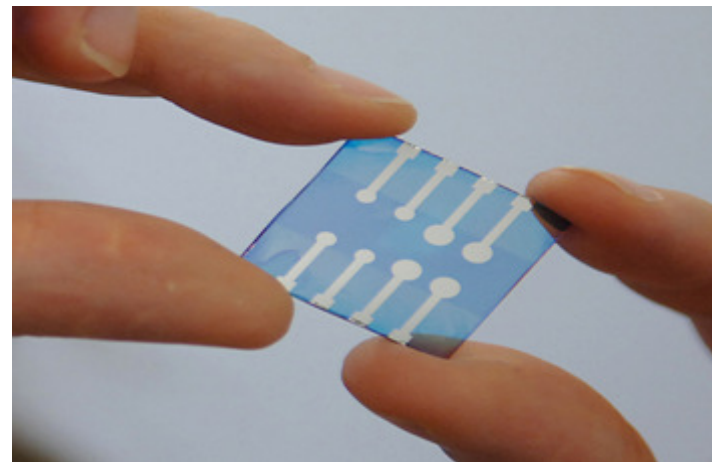
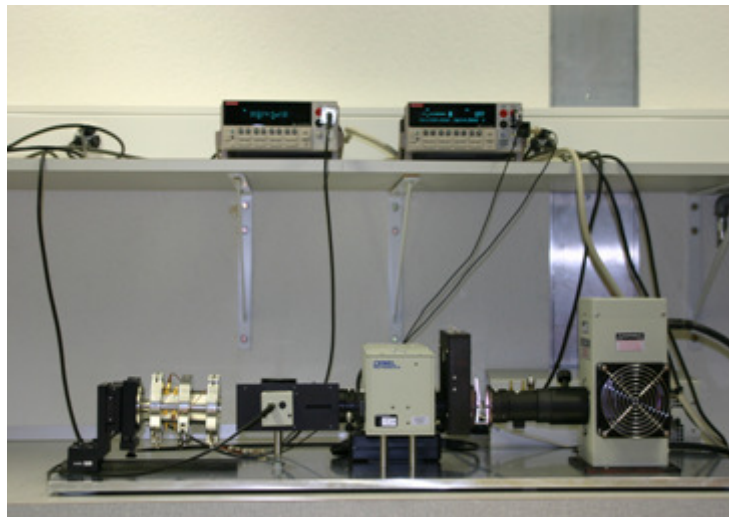
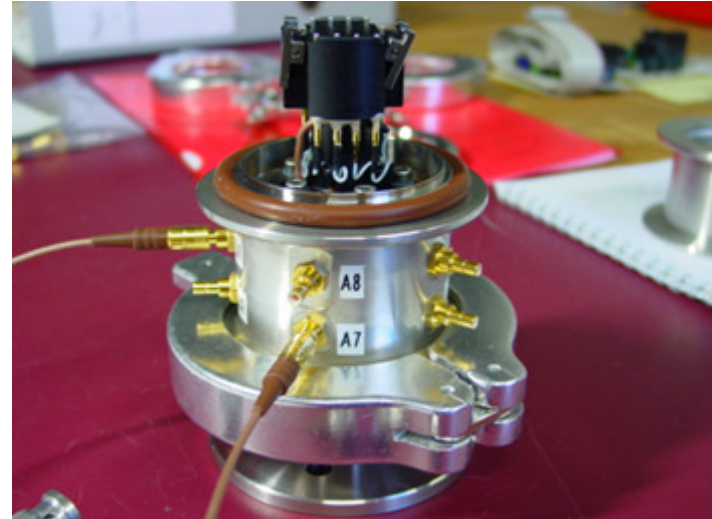
crystallization

thin films – disjoining
pressure

Ionic space charge: SIMS analysis



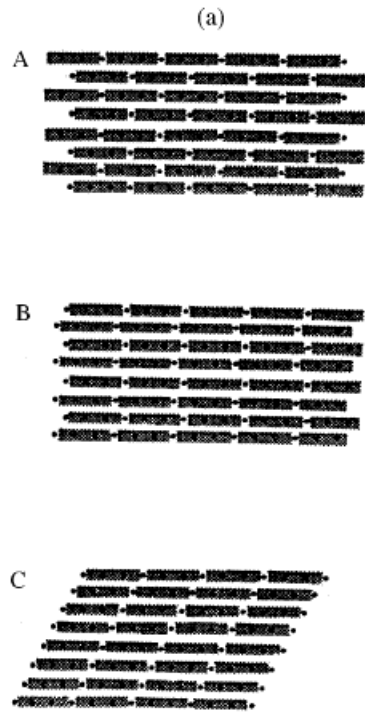
Fabrication process



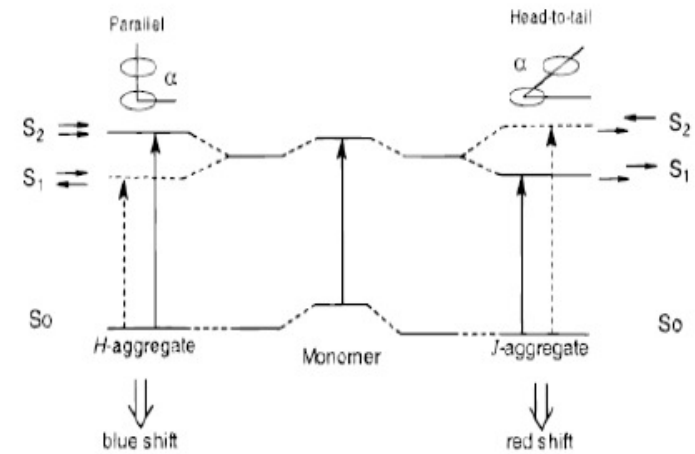
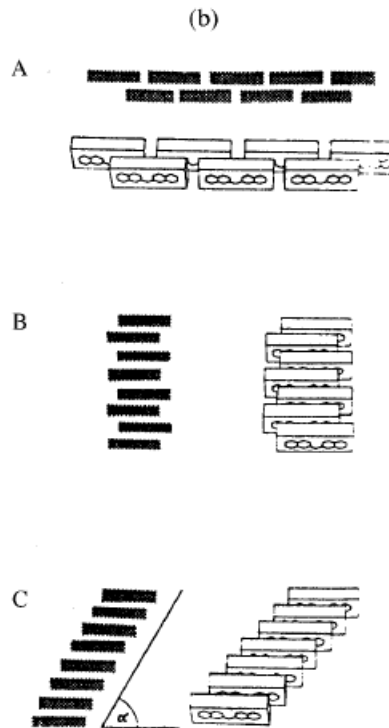
Aggregation of Cyanine Dyes:

- Delocalization of the positive charge on one nitrogen atom
- ⇒ Strong intermolecular van der Waals attractive forces
- ⇒ Aggregation

Adsorbed on a surface:



In solution:



Delocalized electron state
⇒ change in absorption:

$\alpha < 32^\circ$ (large molecular slippage):

⇒ Bathochromic shift (J-band)

$\alpha > 32^\circ$ (small molecular slippage):

⇒ Hypsochromic shift (J-band)