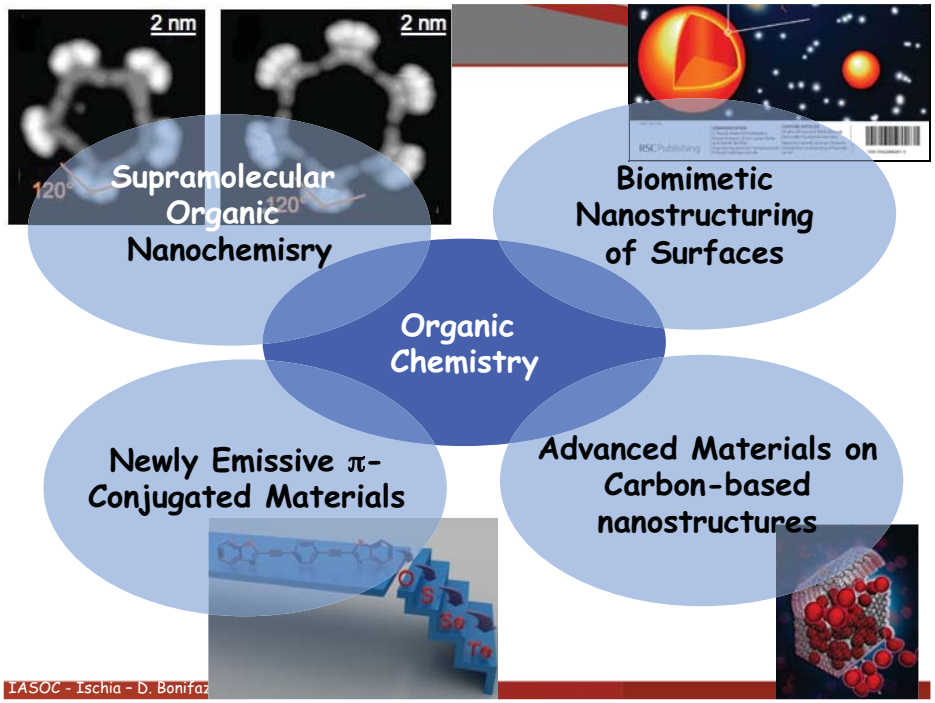
Mastering Organic Matters through Weak Interactions

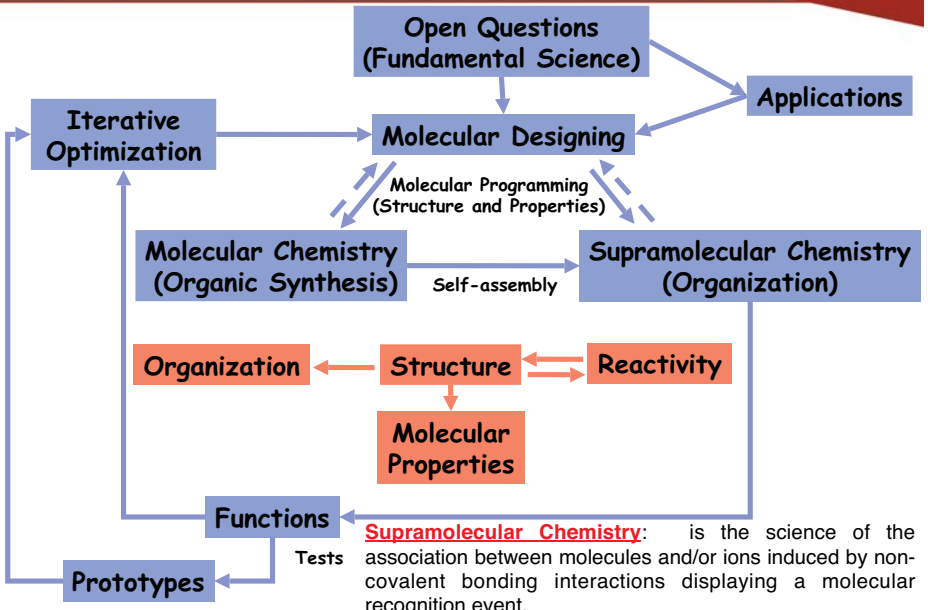
Dr. Davide Bonifazi

Namur Research College (NARC) and Department of Chemistry,
University of Namur (FUNDP), Rue de Bruxelles 61, 5000 Namur, Belgium
&
Department of Chemical and Pharmaceutical Sciences
University of Trieste, Piazzale Europa 1, Trieste, Italy

Ischia Advanced School of Organic Chemistry (IASOC)
Ischia Island (Napoli)

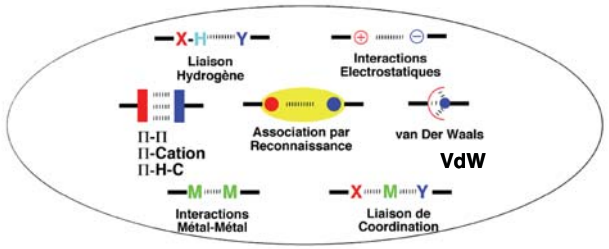


Our Scientific Approach



Supramolecular Chemistry: is the science of the association between molecules and/or ions induced by non-covalent bonding interactions displaying a molecular recognition event.

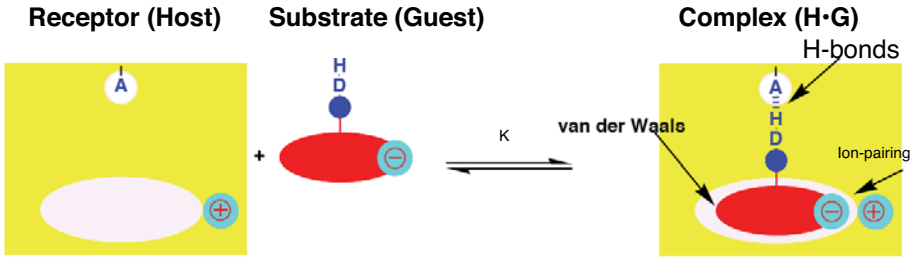
The supramolecular toolbox: weak interactions



Interaction	*E* (KJ mol^{-1})
VdW	<5
π-π	0-30
dipole-dipole	5-50
cation-π	5-80
Halogen-bond (N···I)	20-40
H-bond	4-120
Metal coordination	40-120
Electrostatic	50-200
Covalent bond	200-300

E (Kcal mol^{-1})

Thermodynamics of a molecular recognition event



The interactions we considered so far largely contribute to the **Enthalpy** of the the equilibrium. What about the **Entropy**?

The enthalpies of interactions are relatively weak

⇩

…therefore entropy plays a significant role in self-assembly

⇩

….which means that solvation cannot be disregarded

What is Self-assembly?

Self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by noncovalent bonds

⇩

Self-assembled structures represent <u>thermodynamic minima</u>

Kinetic *vs* Thermodinamic Control

In kinetically controlled reactions the relative magnitude of the transition states determines the product distribution

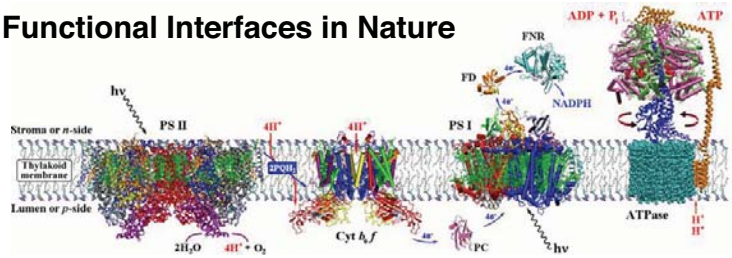
In thermodynamically controlled reactions the relative thermodynamic stabilities of the products are responsible for the product ratio under thermodynamic control

Interfaces at play

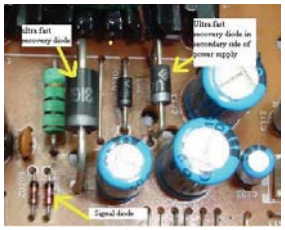
INTERFACE:
the area where two immiscible phases of a dispersion come into contact. It includes also the same or different states of matter.

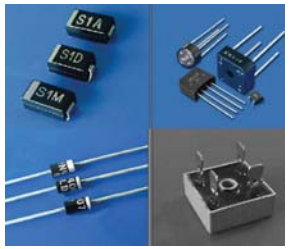
Interfaces at play

Functional Interfaces in Nature

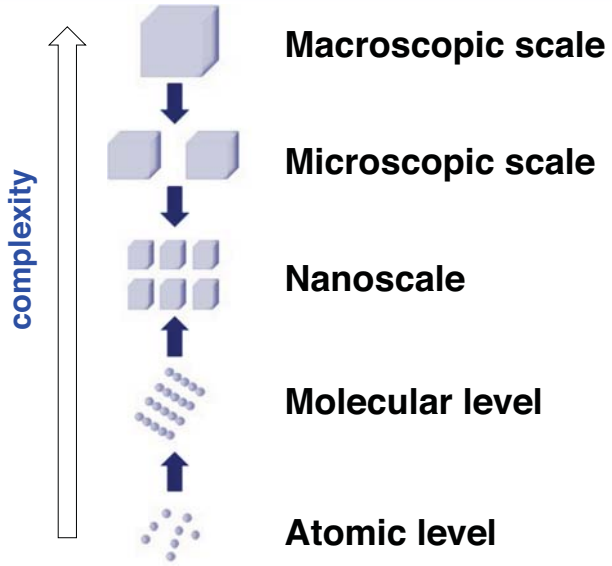


Artificial Functional Interfaces

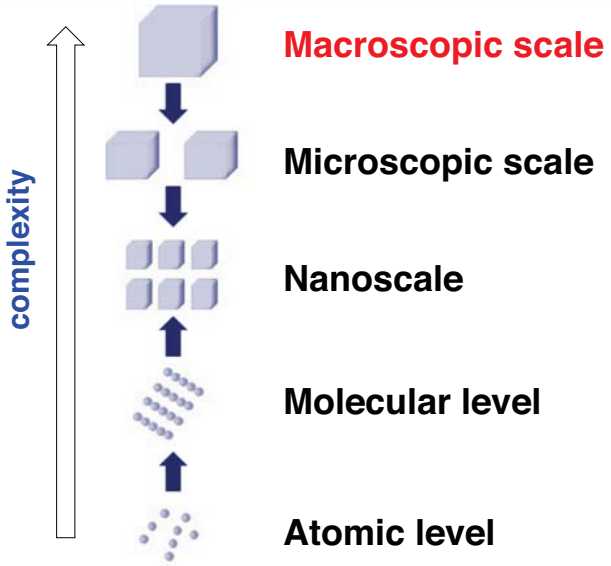




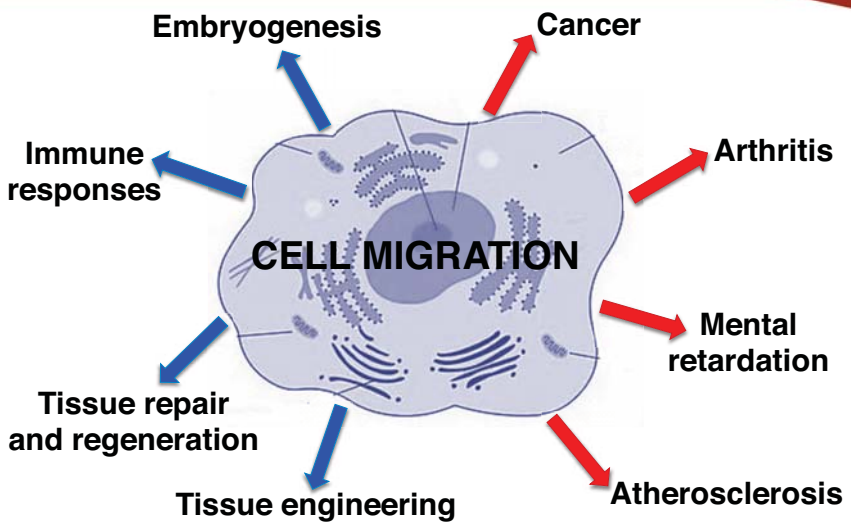
Outline



Outline



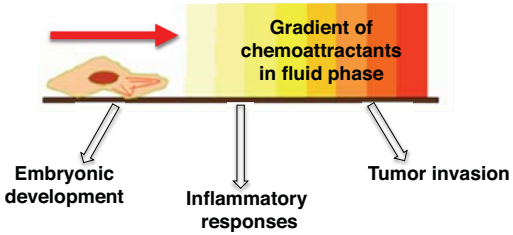
Cellular migration



A. J. Ridley, M. A. Schwartz, K. Burridge, R. A. Firtel, M. H. Ginsberg, G. Borisy, J. T. Parsons, A. R. Horwitz, *Science* **2003**, 302, 1704; P. Friedl, D. Gilmour, *Nature Rev. Mol. Cell. Biol.* **2009**, 10, 445.

Chemotaxis *vs* Haptotaxis

Chemotactic Cellular Migration



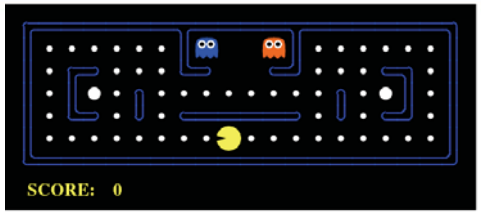
P. Devreotes, C. Janetopoulos *J. Biol. Chem.* **2003**, 278, 20445; P. J. M. Van Haastert *J. Cell. Sci.* **2010**, 123, 3031.

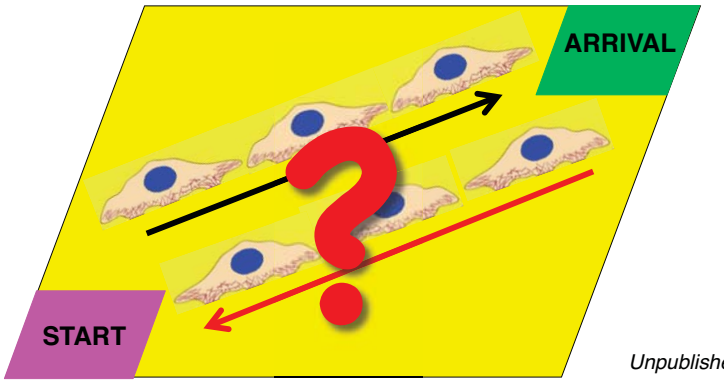
Haptotaxis: chemotaxis along surfaces

J. Genzer, R. R. Bath *Langmuir* **2008**, 24, 2294; B. M. Lamb, D. G. Barret, N. P. Westcott, M. N. Yousaf *Langmuir* **2008**, 24, 8885.

The «Pacman project»

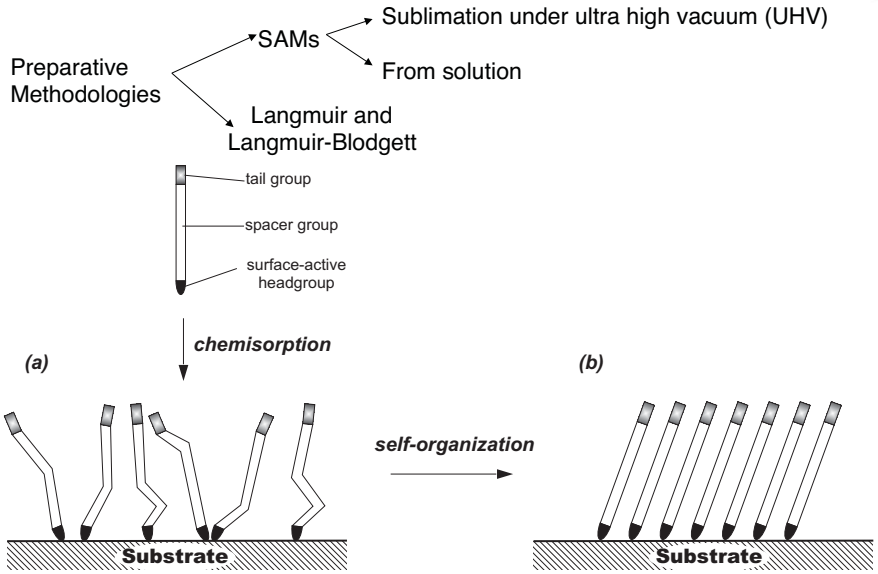
R. Marega



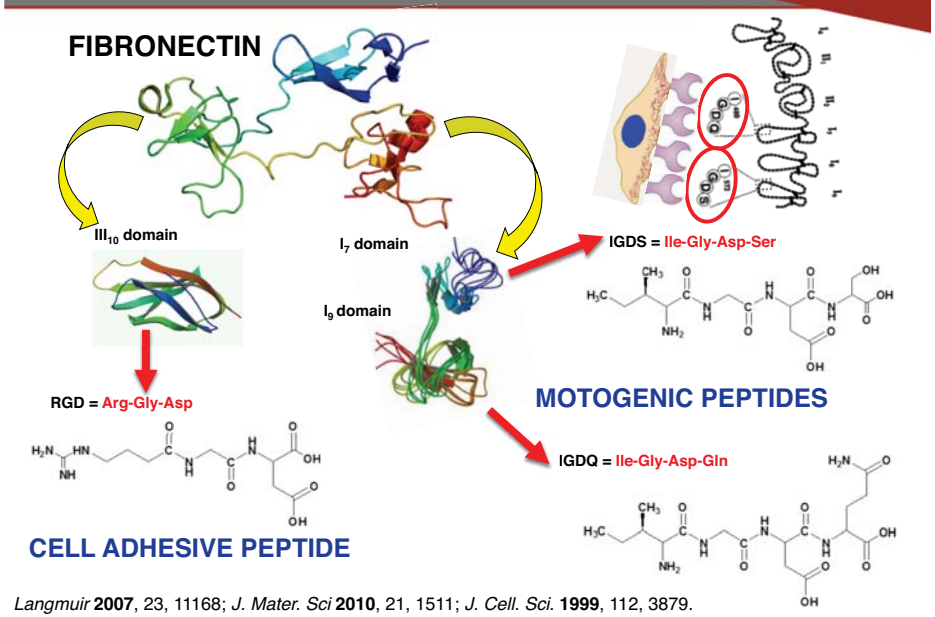


Unpublished results

Self-assembled Monolayers (SAMs) on Surfaces



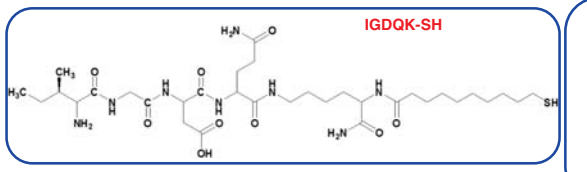
Motogenic IGD sequences



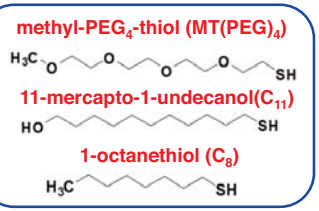
Langmuir **2007**, 23, 11168; *J. Mater. Sci* **2010**, 21, 1511; *J. Cell. Sci.* **1999**, 112, 3879.

IGDQK-SH chemical gradient

➢ ***Mixed gradient SAMs***



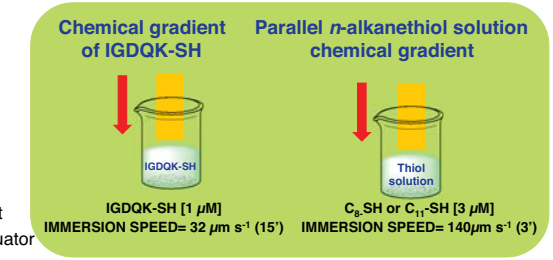
***n*-alkanethiols**



➢ ***Chemical gradient generation***

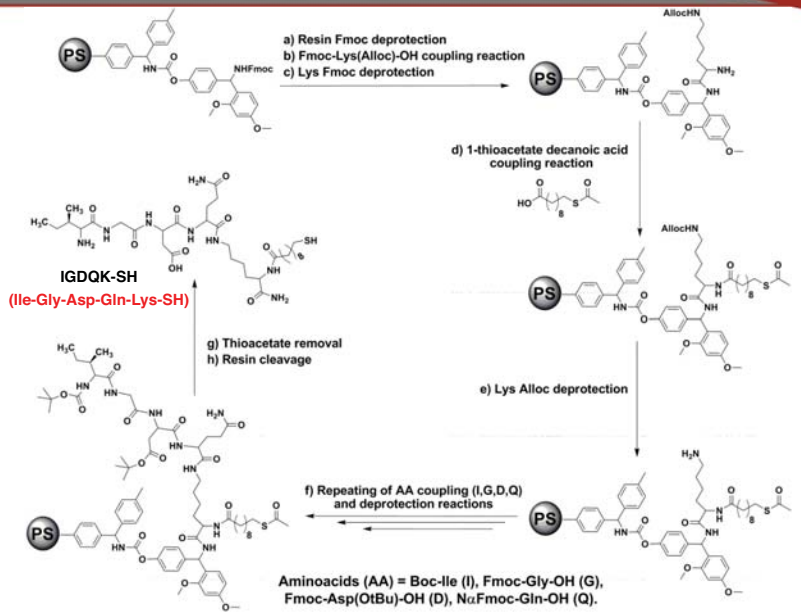
- 1D
- dynamic
- directional chemical gradient on few mm-scale

Schematic representation of the gradient generation through the action of a linear actuator



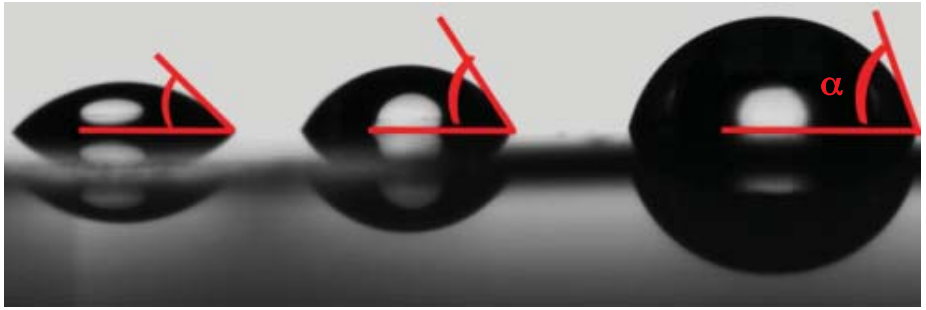
S. Morgenthaler, S. W. Lee, S. Zurcher, N. D. Spencer, *Langmuir* **2003**, 19, 10459

Synthesis of IGDQK-SH



Characterization: wettability

Water contact angle (WCA, α)

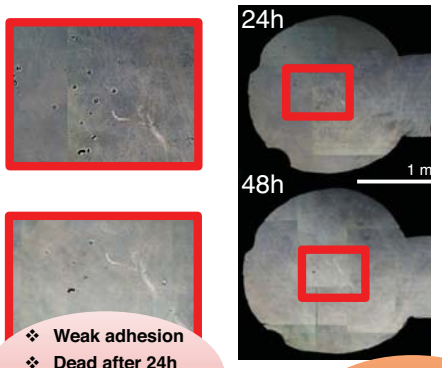


SAMPLE	1 mm	5 mm	9 mm	Δ
G15C – G3MT(PEG)$_4$	37.9 ± 0.3	40.6 ± 1.1	45.0 ± 1.4	7.1
G15C -G3C$_{11}$OH	68.3 ± 0.7	58.5 ± 2.7	39.6 ± 1.0	-28.7
G15C – G3C$_8$	48.7 ± 1.0	59.3 ± 0.7	71.2 ± 0.7	22.5

Cellular migration studies

MT(PEG)$_4$

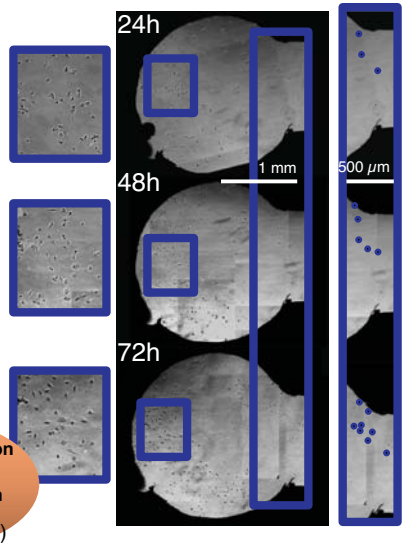
IGDQK-SH chemical gradient with full immersion into MT(PEG)$_4$ solution



- Weak adhesion
- Dead after 24h
- No replication
- No migration

- Good adhesion
- Mostly alive
- No replication
- No migration

IGDQK-SH chemical gradient with pallalel gradient into MT(PEG)$_4$ solution

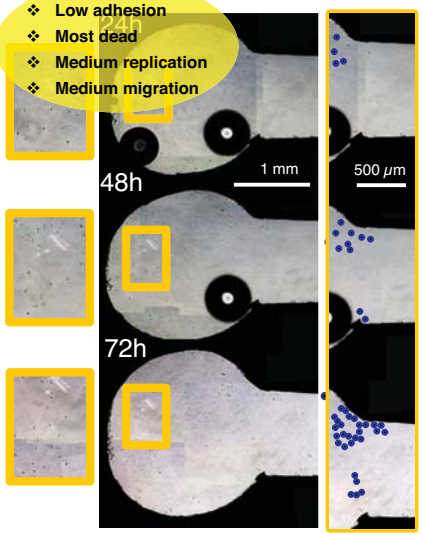


Endothelial cells (Ahy926) in glucose (DMEM 4.5 g/L)

Cellular migration studies

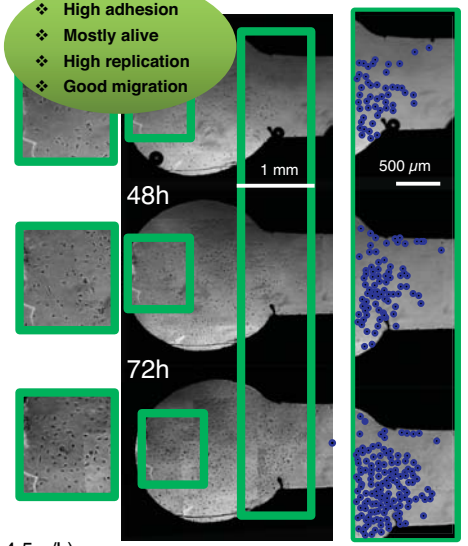
IGDQK-SH chemical gradient + C$_{11}$

- Low adhesion
- Most dead
- Medium replication
- Medium migration



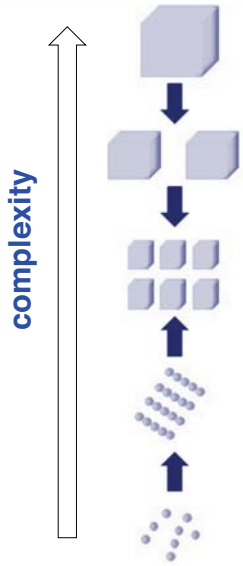
IGDQK-SH chemical gradient + C$_8$

- High adhesion
- Mostly alive
- High replication
- Good migration



Endothelial cells (Ahy926) in glucose (DMEM 4.5 g/L)

Outline



Macroscopic scale

Microscopic scale

Nanoscale

Molecular level

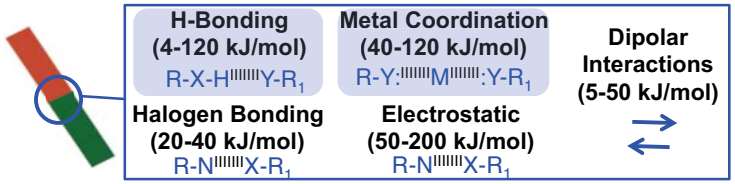
Atomic level

The approach

- **Multi-component:** angular unit: control of the shape & linear unit: control of the size
- **Pre-organization**: fixed geometry of the molecules

Assembling Units	180°	60°	120°	90°
180°				
180°				

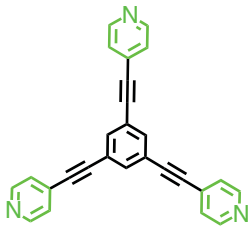
- **Directional Recognition:** non-covalent highly-directional interactions

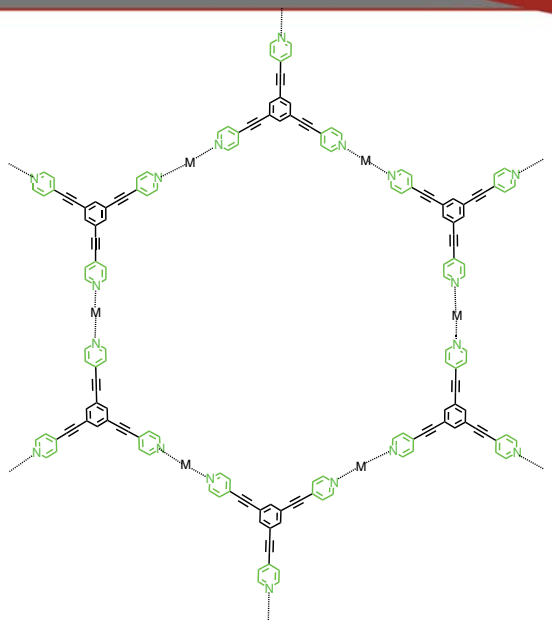


Chem. Eur. J. **2009**, *15*, 7004; *Coord. Chem. Rev.* **2010**, *254*, 2342.

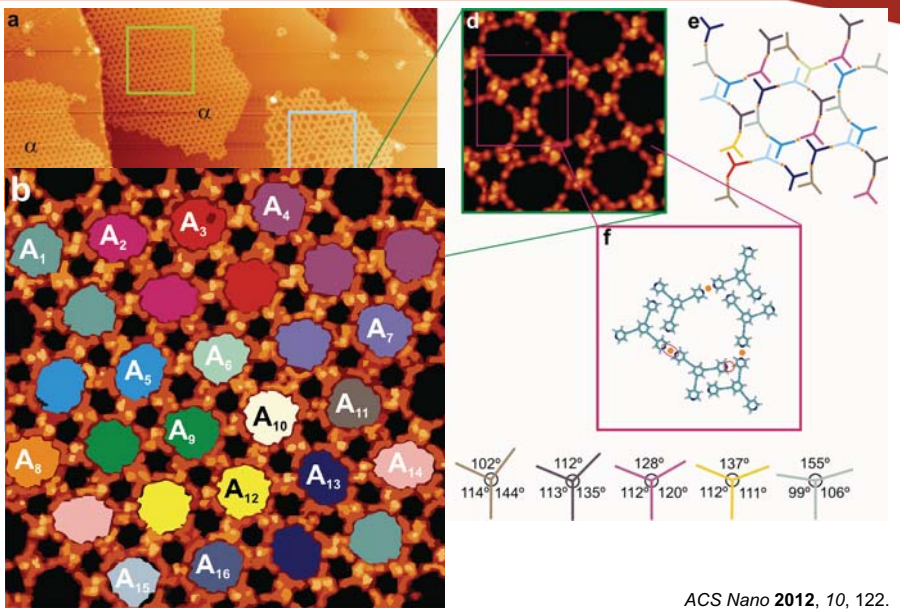
Towards 2D infinite predictable porous networks…

C. Aurisicchio



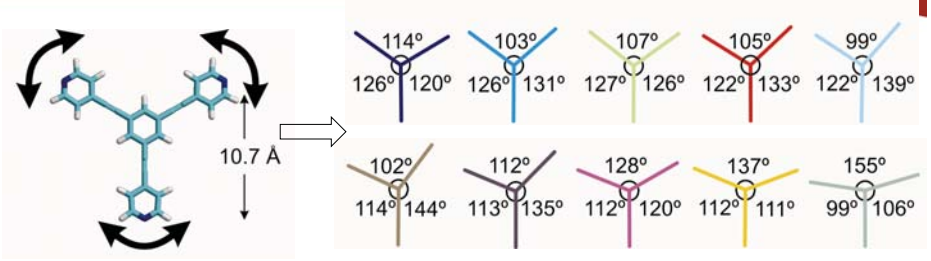


Porous patterned surfaces



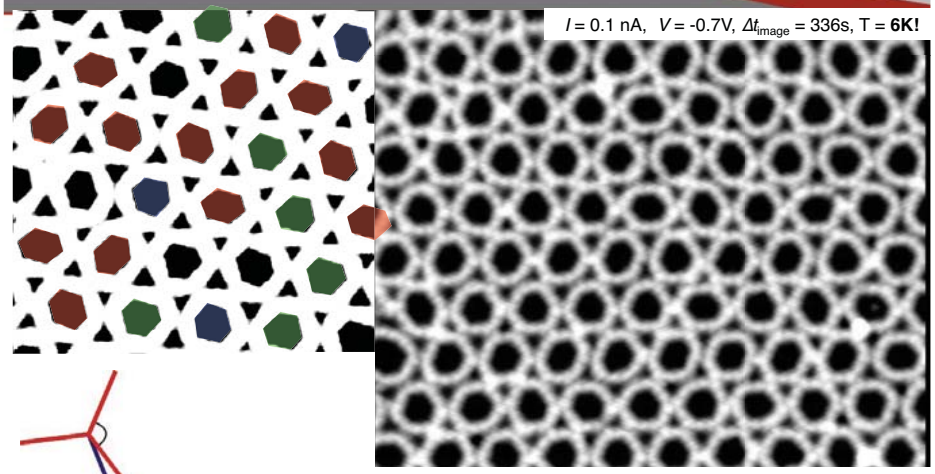
ACS Nano **2012**, *10*, 122.

Conformations or Configurations?



According to Ernest Ernest L. Eliel and Samuel H. Wilen in *Stereochemistry of Organic Compounds* (1994, p. 20-19), "***the most fundamental distinction one can make between configuration and conformation is to say that configurational differences imply differences in bond angles, whereas conformational differences involve differences in torsion angles (including in both case, differences, that are exclusively in sign).***" Based on this distinction, isolable molecules of identical constitution but differing in bond angles under the chosen "instrumental conditions" can be thus discussed a configurational isomers.

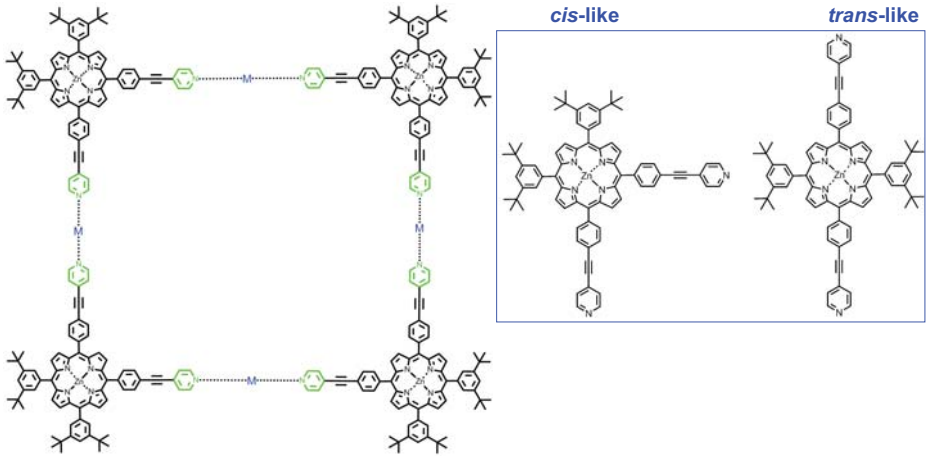
Breathing pores



Breathing obtained while scanning at I = 0.1 nA, V= -0.7V, at 6K. Causes: **Flipping of legs**: flexibility, altogether with some rotation of the pyridyls and **N-H bonding changing** between molecules of adjacent pores.

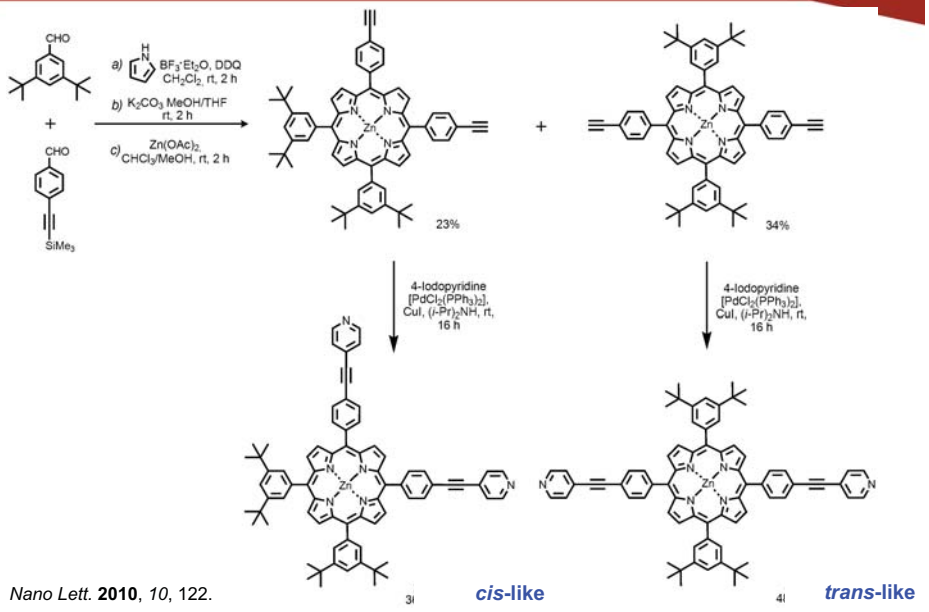
Discrete assemblies

Discrete square-like assemblies engineered through metal coordination interaction betwenn disubstituted-pyridyl porphyrins



Nano Lett. **2010**, *10*, 122.

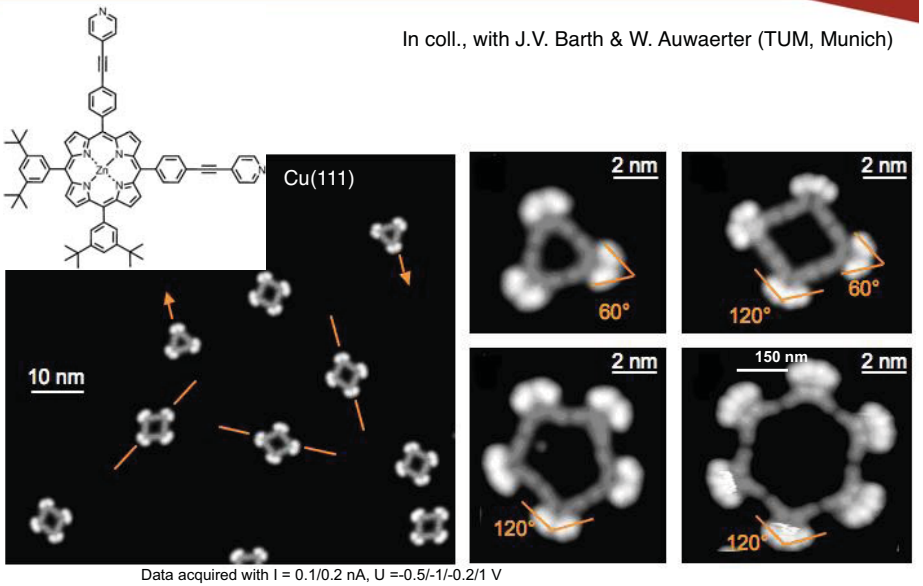
Synthetic Route



Nano Lett. **2010**, *10*, 122.

Surface-assisted Macrocyclization

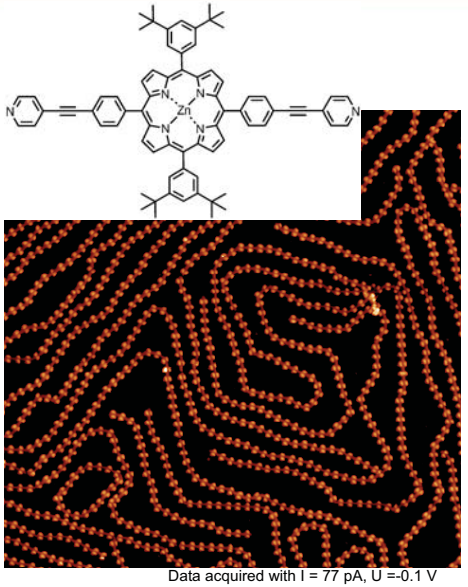
In coll., with J.V. Barth & W. Auwaerter (TUM, Munich)



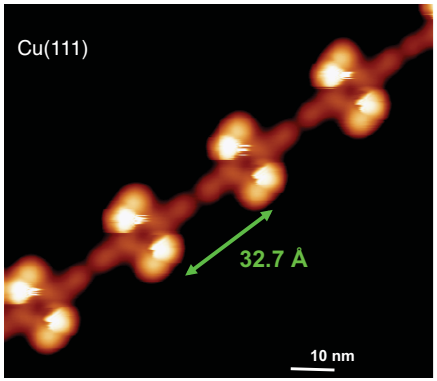
Data acquired with I = 0.1/0.2 nA, U =-0.5/-1/-0.2/1 V

Nano Lett. **2010**, *10*, 122.

Surface-assisted supramolecular wiring



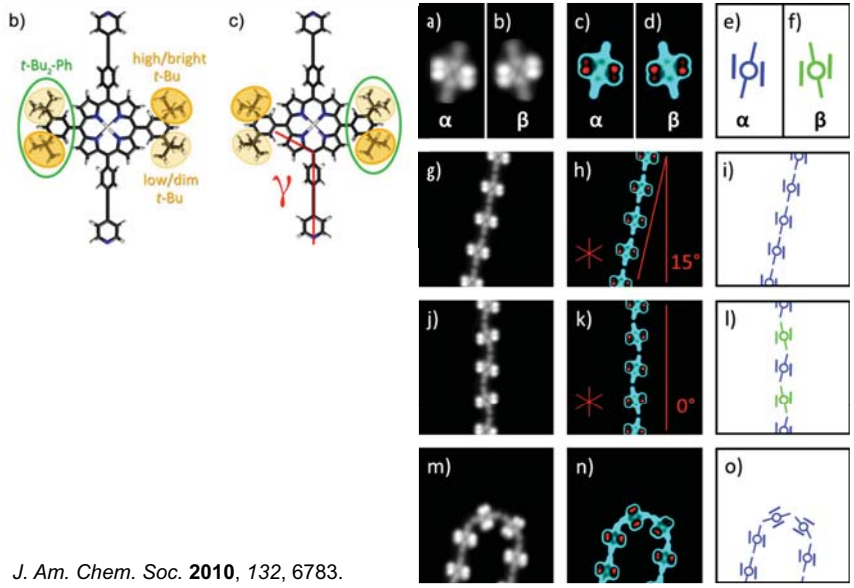
Data acquired with I = 77 pA, U =-0.1 V



Data acquired with I = 77 pA, U =-0.1 V

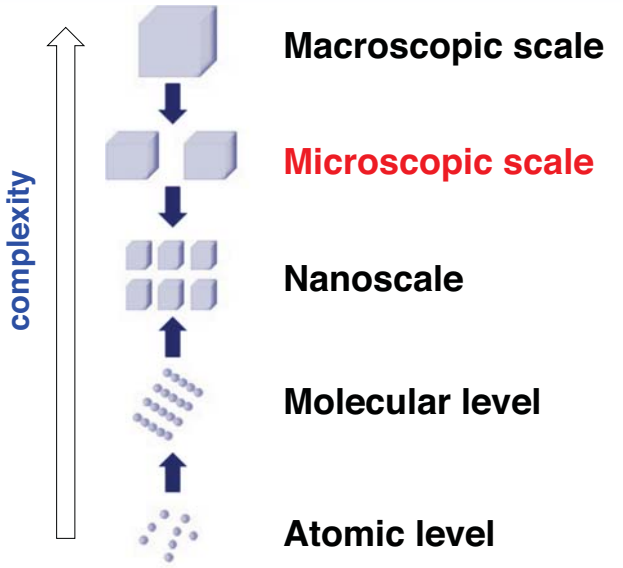
J. Am. Chem. Soc. **2010**, *132*, 6783.

Surface-induced Atropoisomers



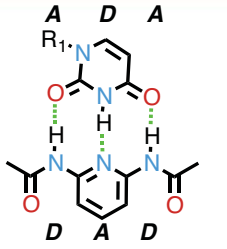
J. Am. Chem. Soc. **2010**, *132*, 6783.

Outline

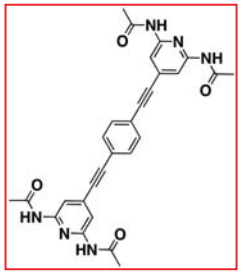


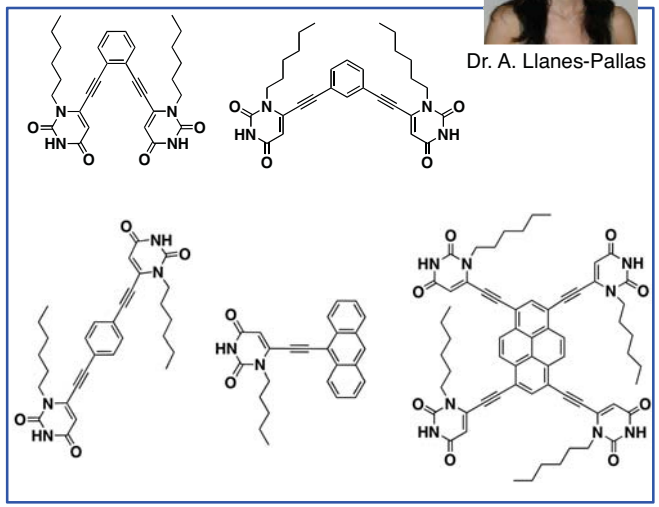
H-bonded supramolecular polymers

Dr. A. Llanes-Pallas



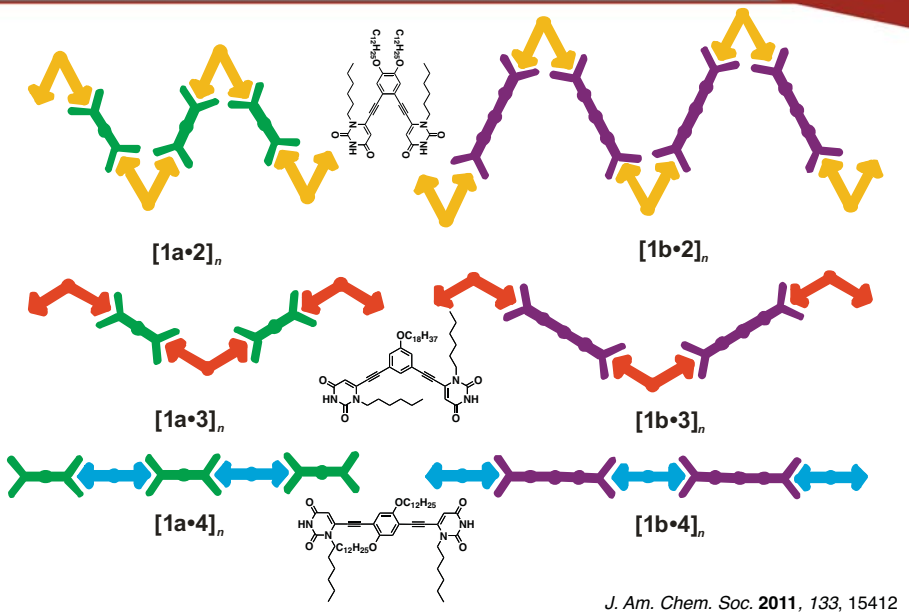
J. Chem. Soc. Chem. Commun., **1994**, *42*, 197





Angew. Chem. Int. Ed. **2008**, *41*, 7726; *J. Am. Chem. Soc.* **2009**, *131*, 509; *J. Am. Chem. Soc.* **2009**, *131*, 13062; *Chem. Commun.* **2009**, 3525; **HOT PAPER**; *Adv. Funct. Mater.* **2009**, *19*, 1207.

H-bonded supramolecular polymers



J. Am. Chem. Soc. **2011**, *133*, 15412

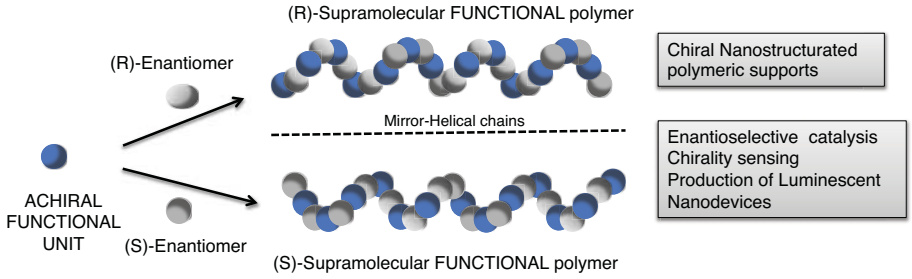
Shaping Objects

T. Marangoni

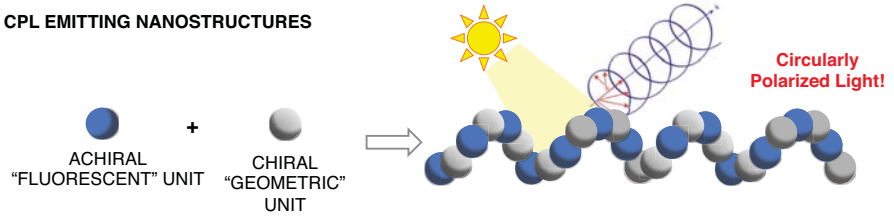
Chem. Commun. **2009**, 2830; *Chem. Eur. J.* **2011**, *17*, 3262; *Nanoscale* **2012**, *in press*

From molecular to microscopic chirality

CONCEPTUAL STRATEGY



CPL EMITTING NANOSTRUCTURES



Thanks to All!!!!

"*If you think that education is expensive, try ignorance* - D. Bok"