Mastering Photoactive Materials through Self-Assembly

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The Abdus Salam International Centre for Theoretical Physics
50th Anniversary 1964-2014

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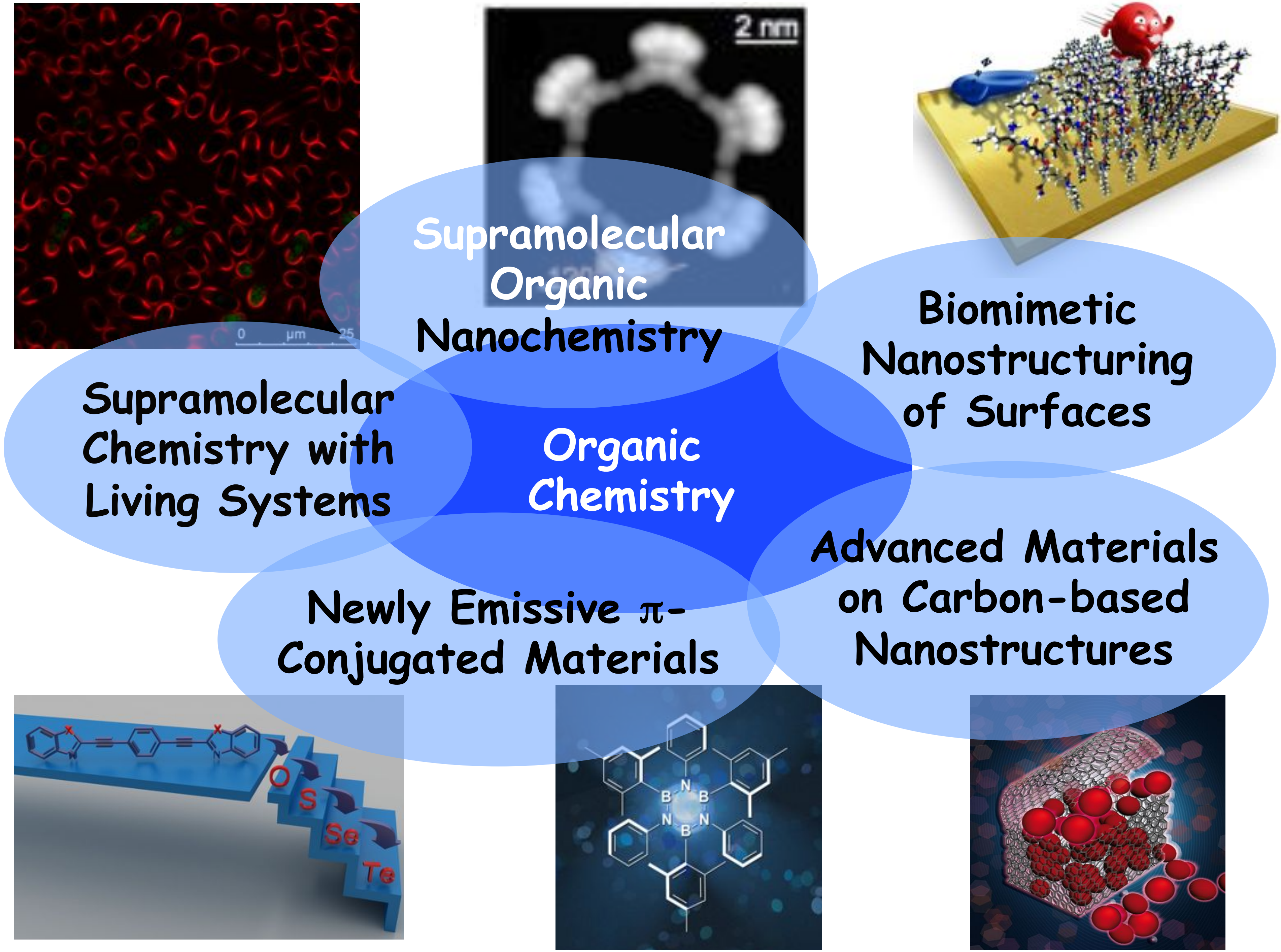
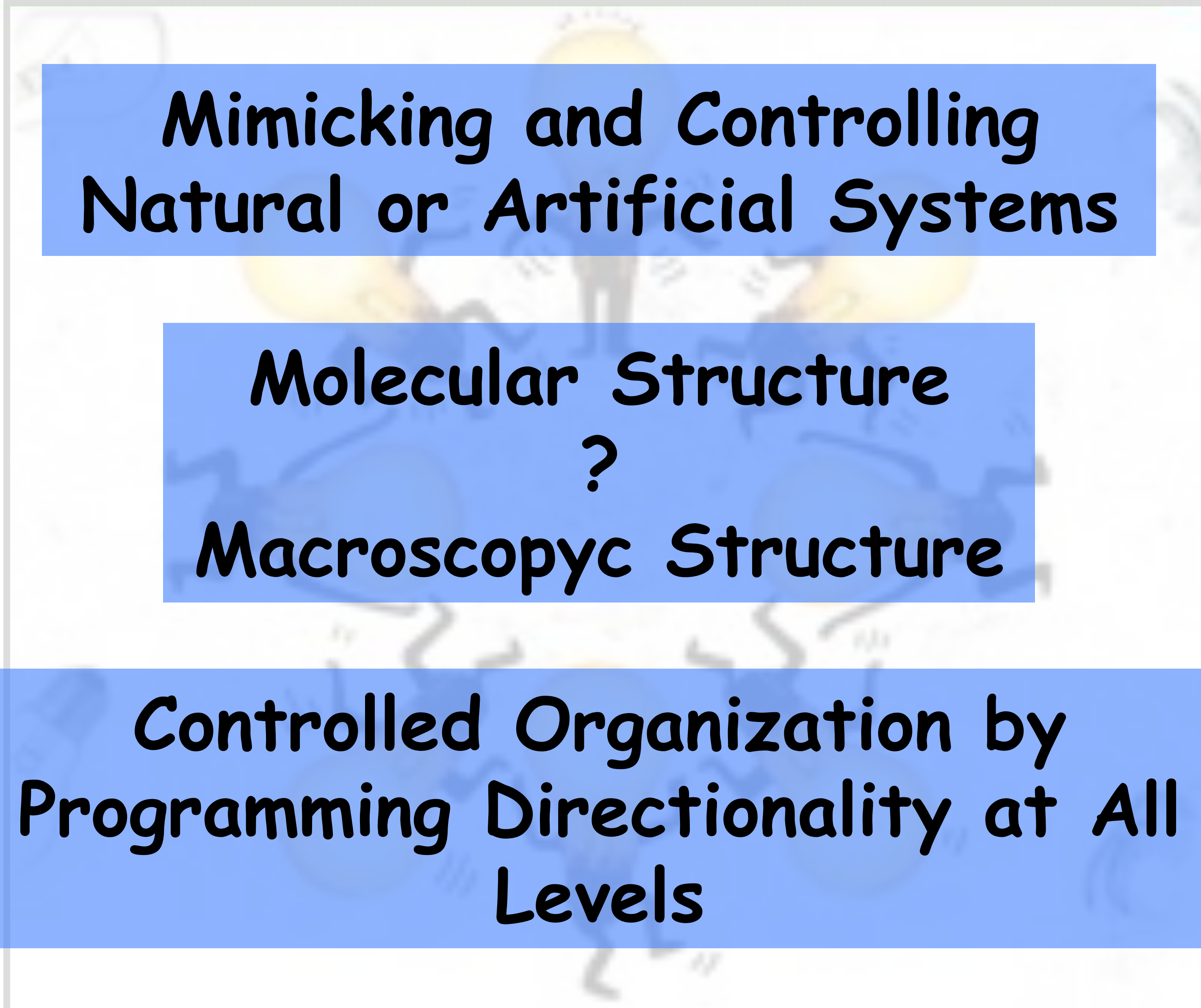


Supramolecular Organic Nanochemistry
Biomimetic Nanostructuring of Surfaces
Supramolecular Chemistry with Living Systems
Organic Chemistry
Advanced Materials on Carbon-based Nanostructures
Newly Emissive π-Conjugated Materials
2 nm
0 µm 25
O
S
Se
Te



Mimicking and Controlling Natural or Artificial Systems

Molecular Structure
?
Macroscopyc Structure

Controlled Organization by Programming Directionality at All Levels

An hierarchical approach

Submolecule

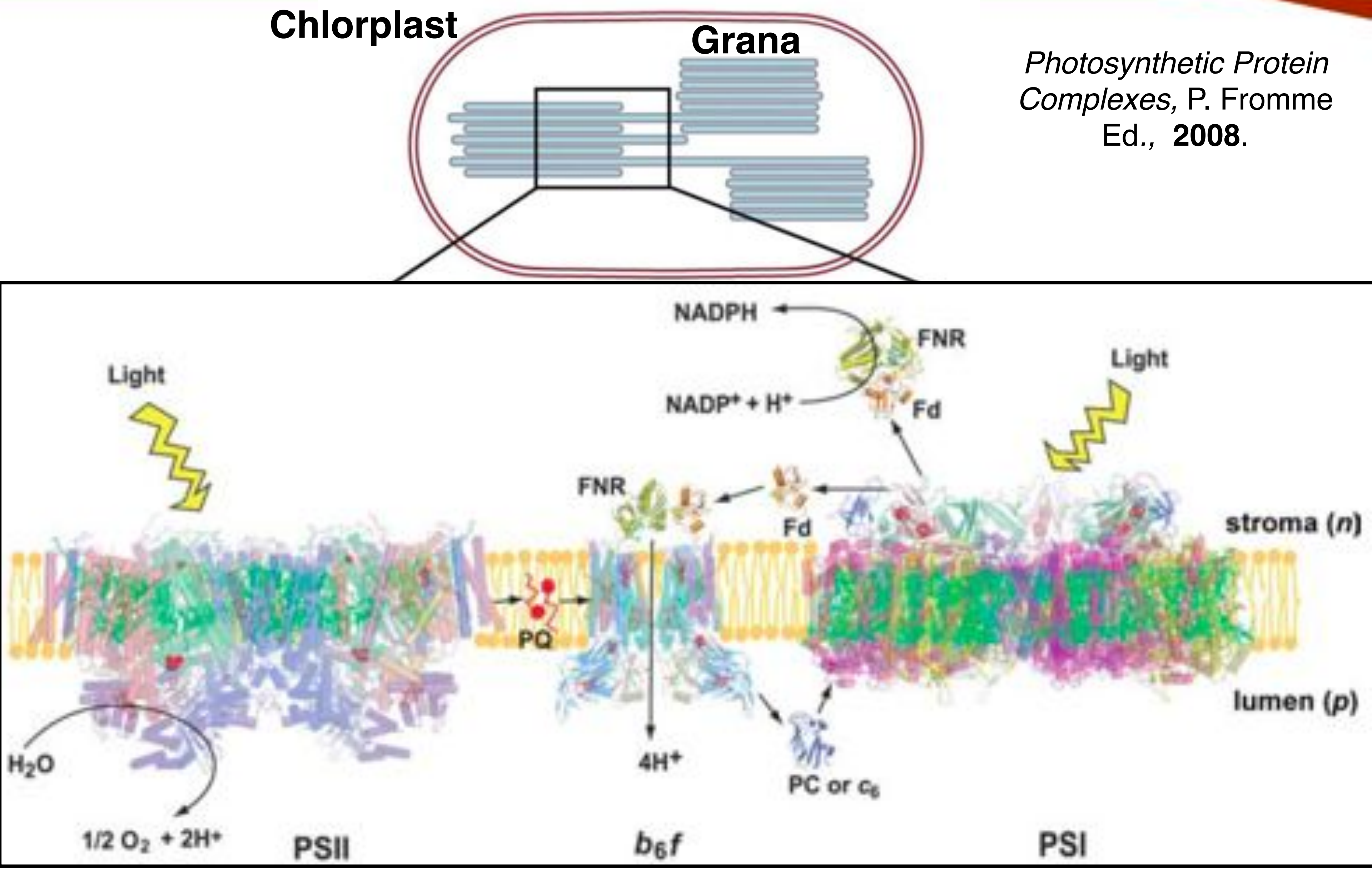
Molecule

Supramolecule

Nano and Micro level

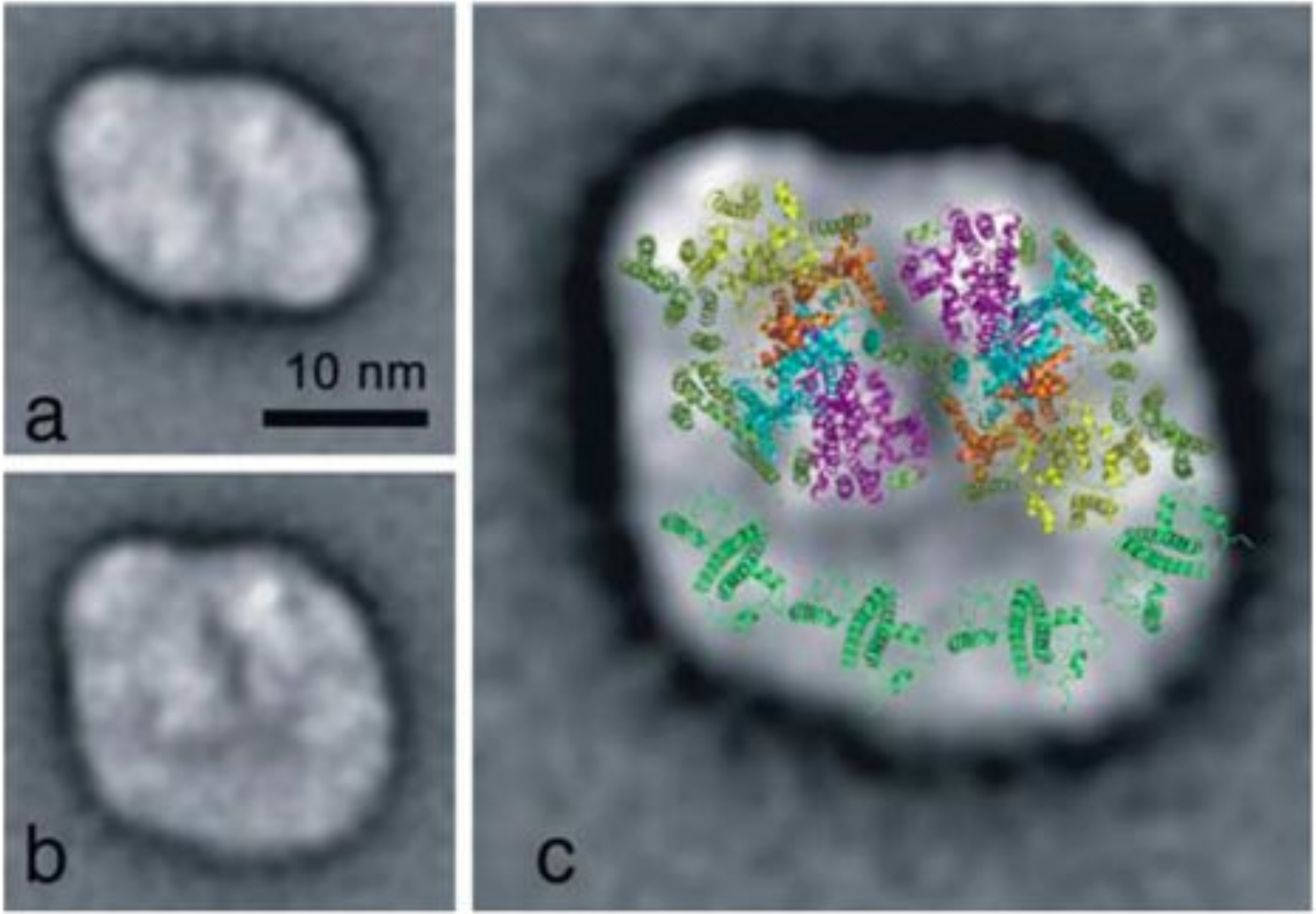
Macroscopic functions

Thylakoid membrane organization: the PSII and PSI system

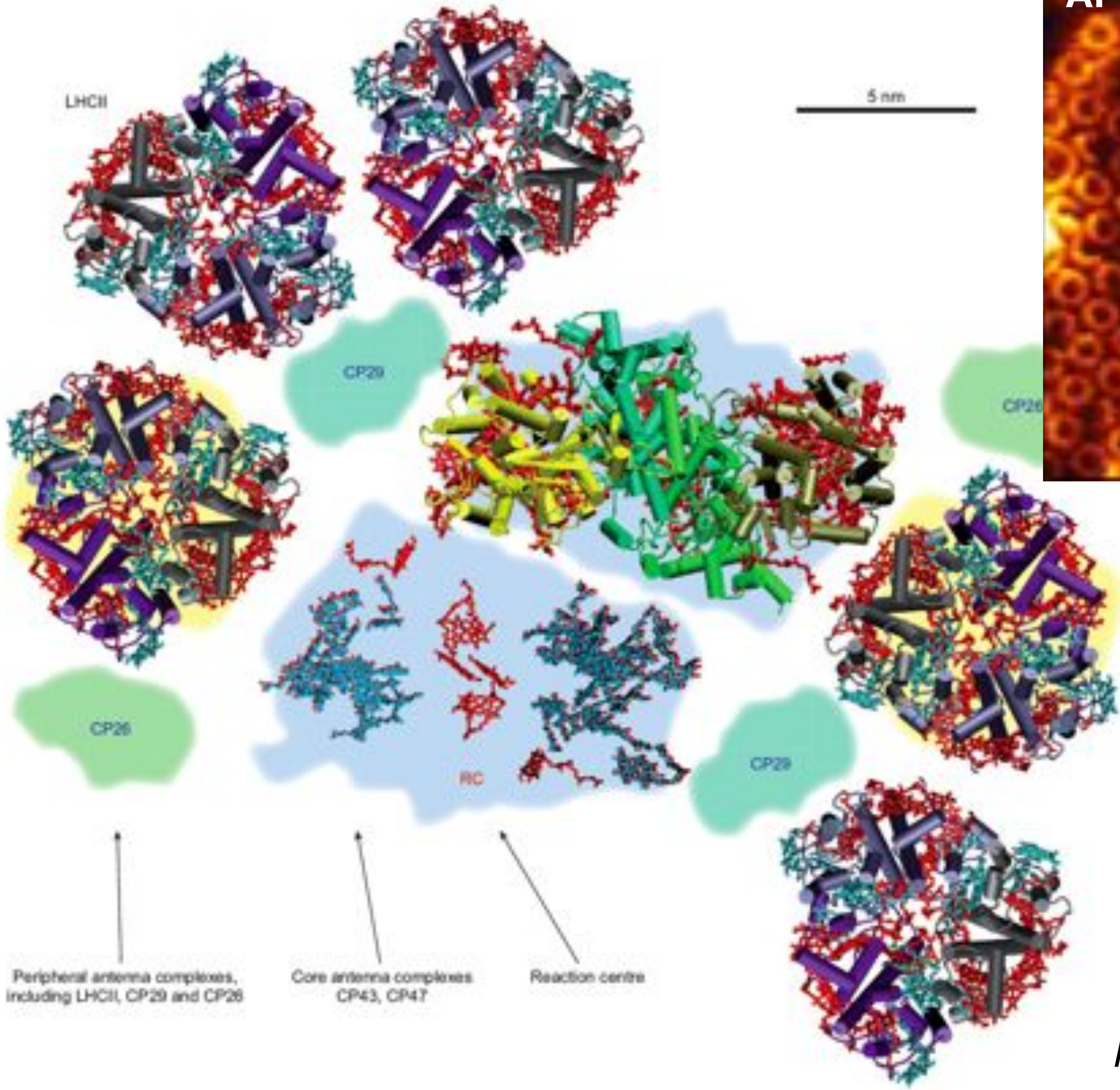


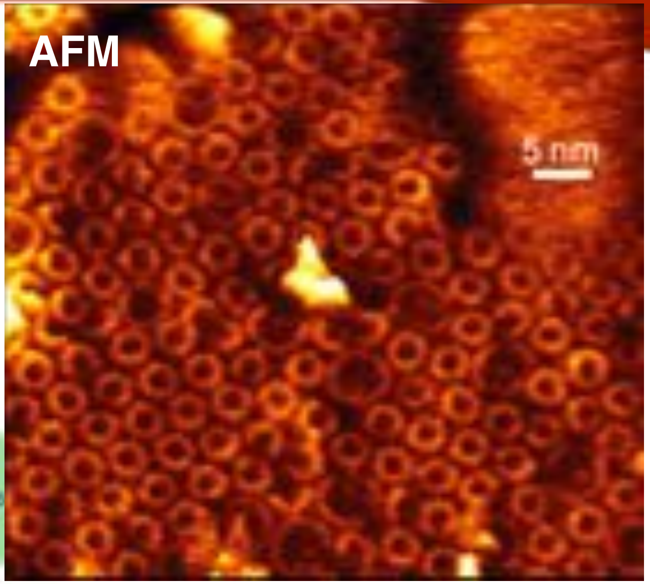
Photosynthetic Protein Complexes, P. Fromme Ed., **2008**.

Electron microscopy projection of a PSII core & LHC complexes



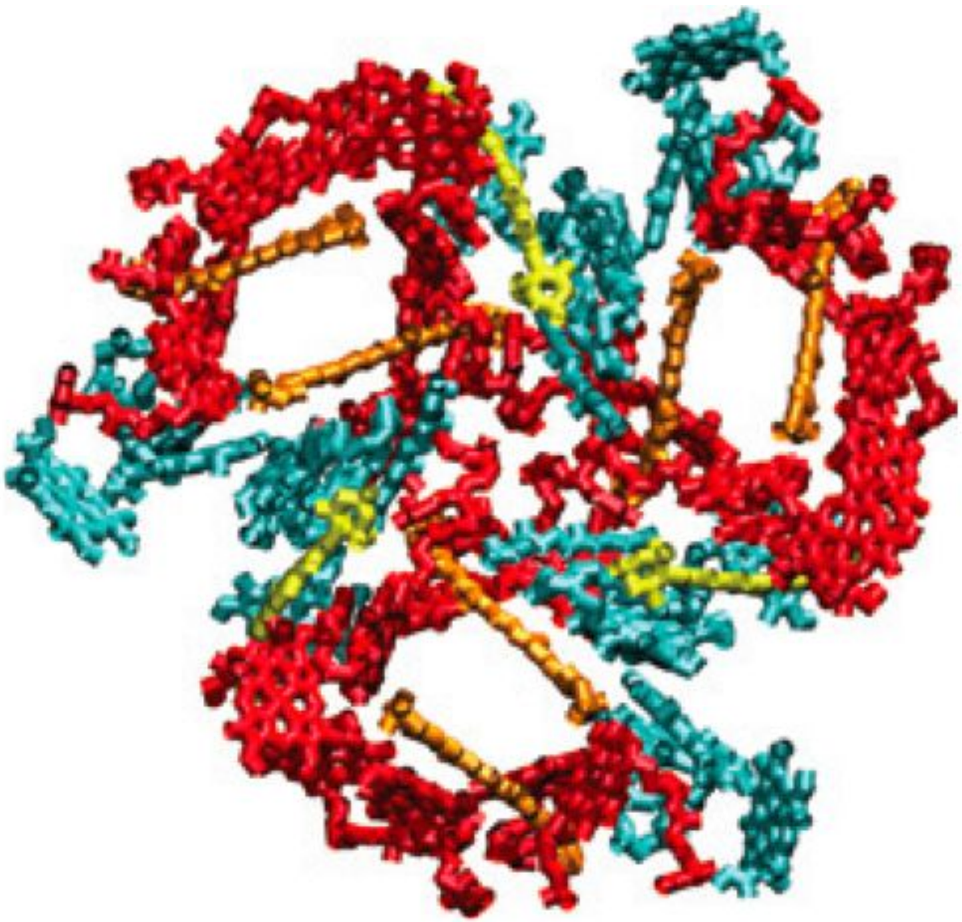
Structural organization of photosystem II (PSII) in higher plants





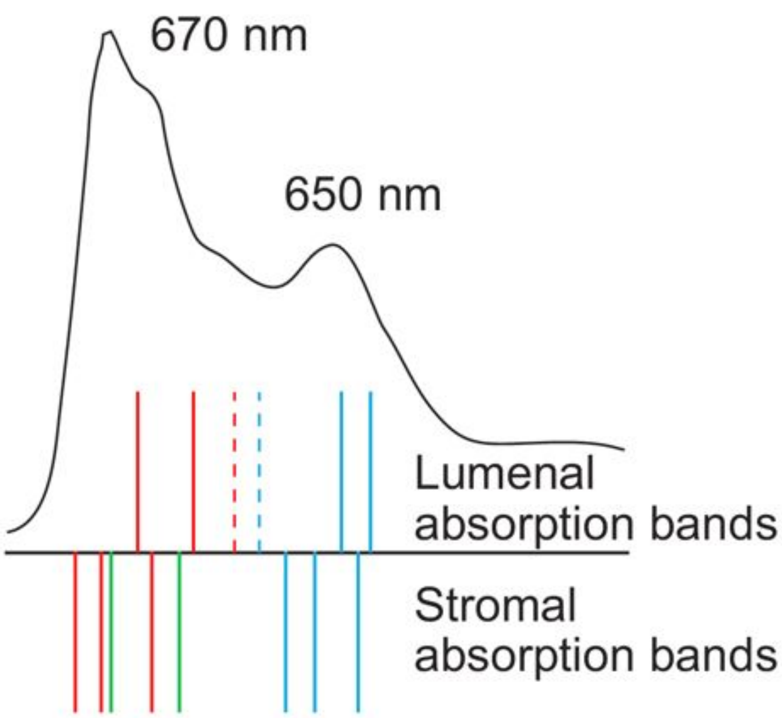
Nature Chem. **2011**, *3*, 763

Structural and light-absorption characteristics of a LCHII



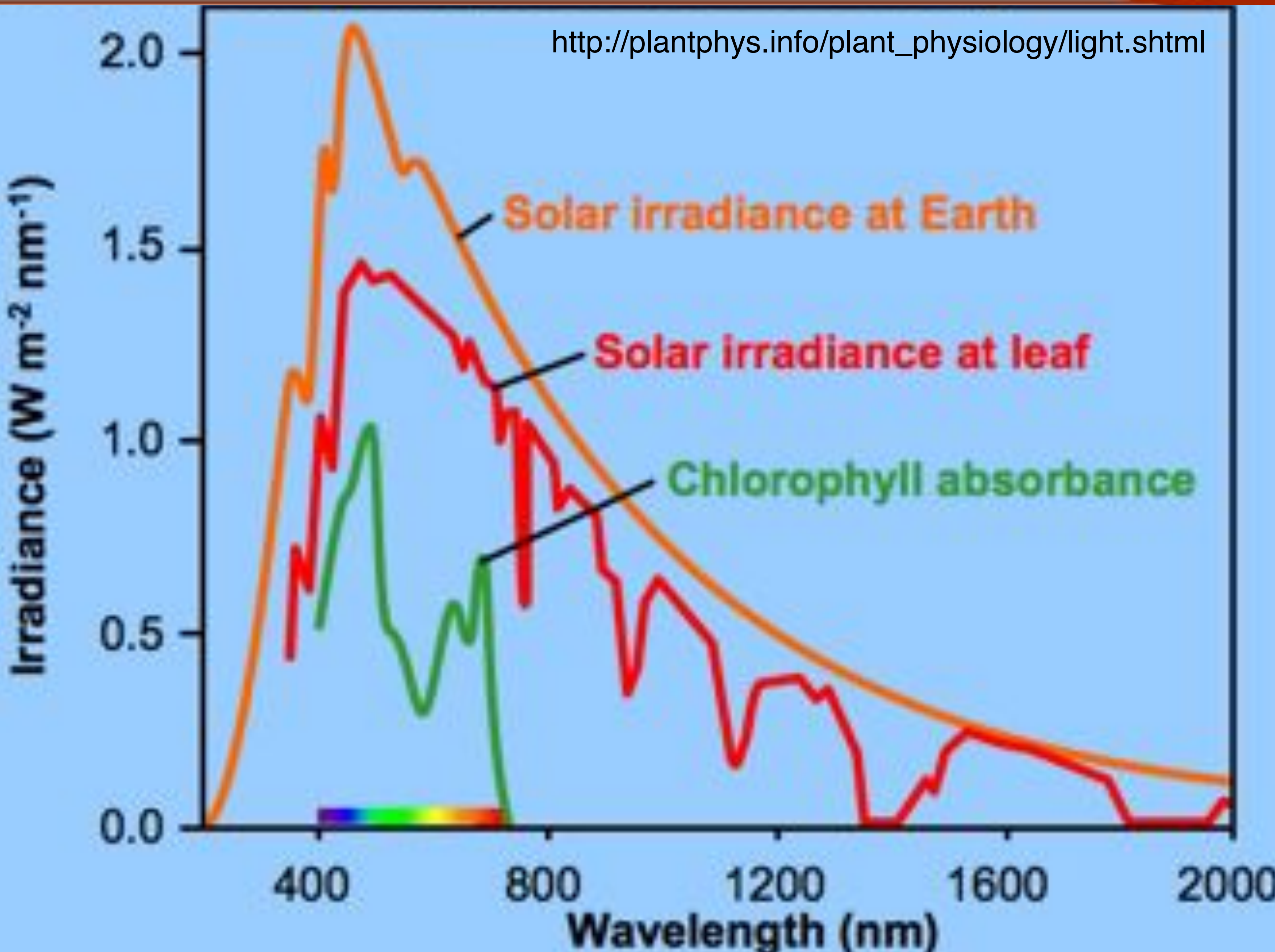
Chlorophyll-a (RED) Chlorophyll-b (BLUE)
Lutein (ORANGE) Violoxanthin (YELLOW)
(the neoxanthin is omitted)

UV-vis absorption spectrum at 77K

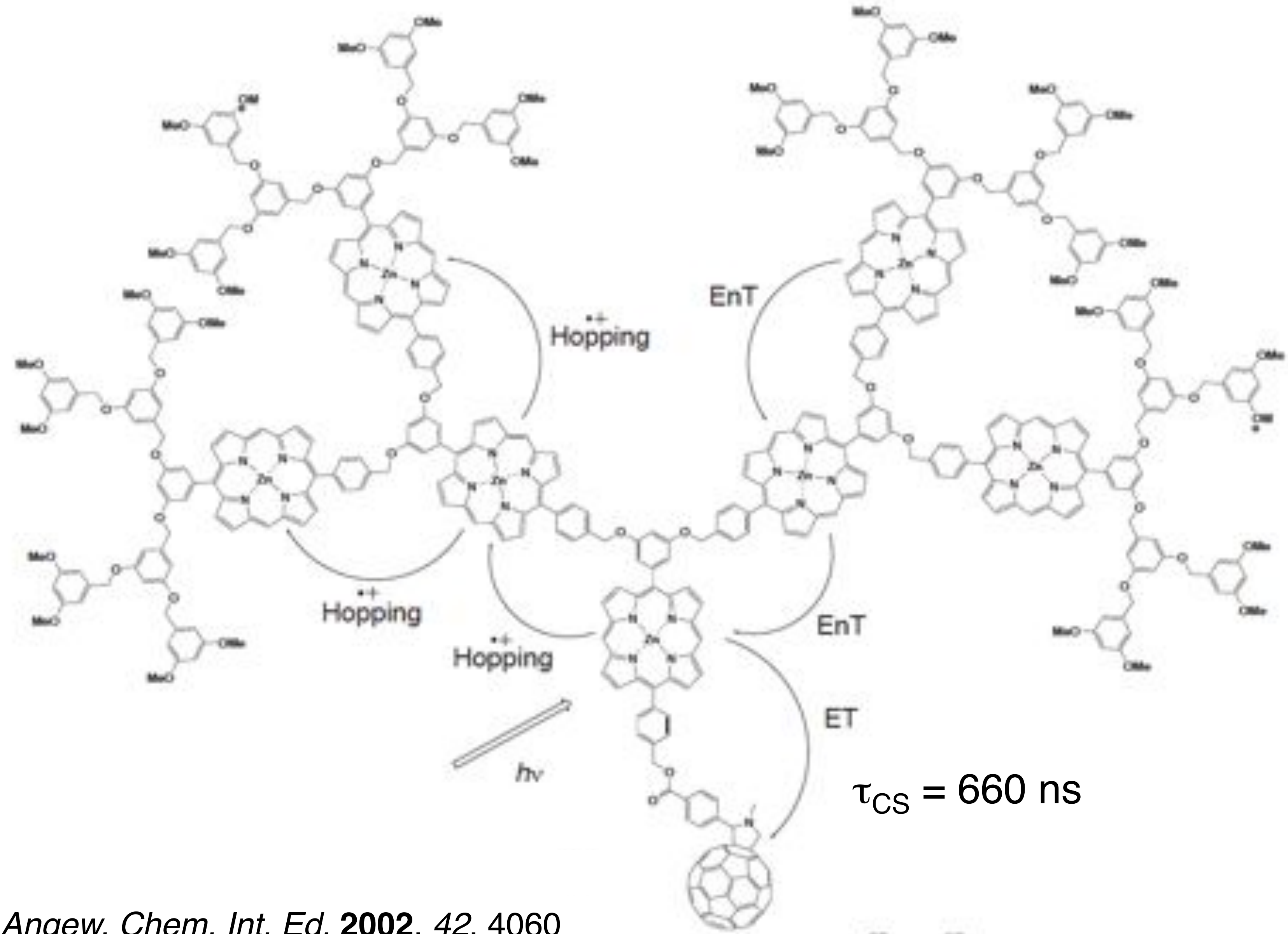


Nature Chem. **2011**, *3*, 763

Solar Energy vs Plant absorbance



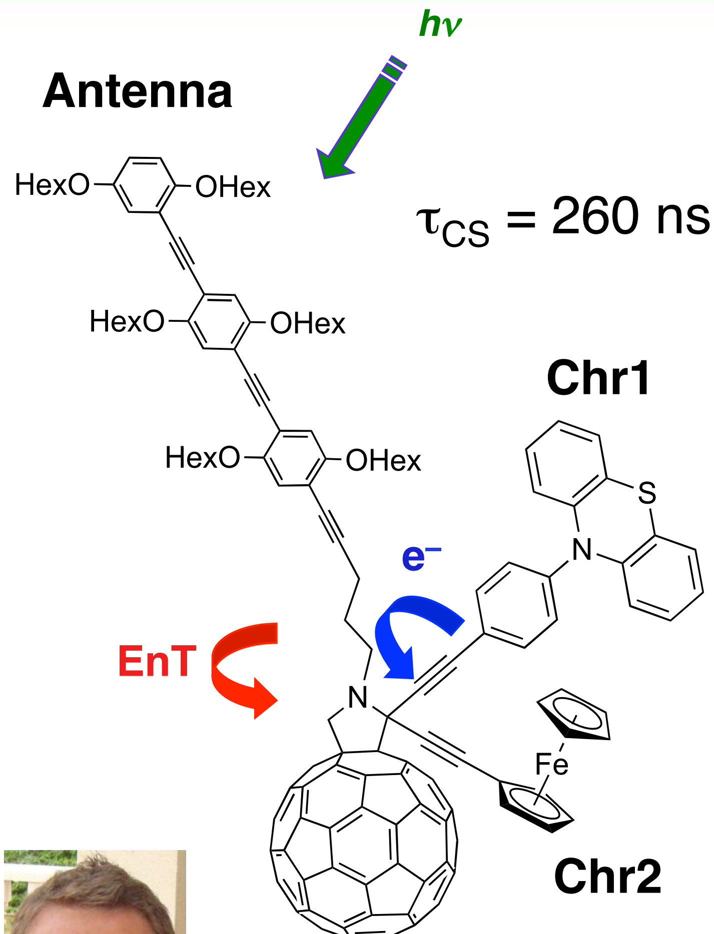
Mimicking photosynthetic reaction centers



τ_{CS} = 660 ns

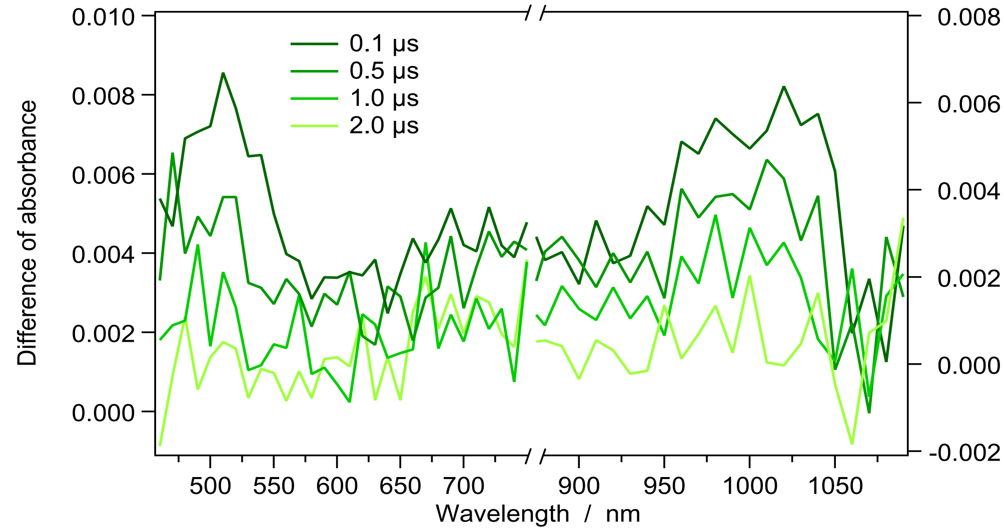
Angew. Chem. Int. Ed. **2002**, *42*, 4060

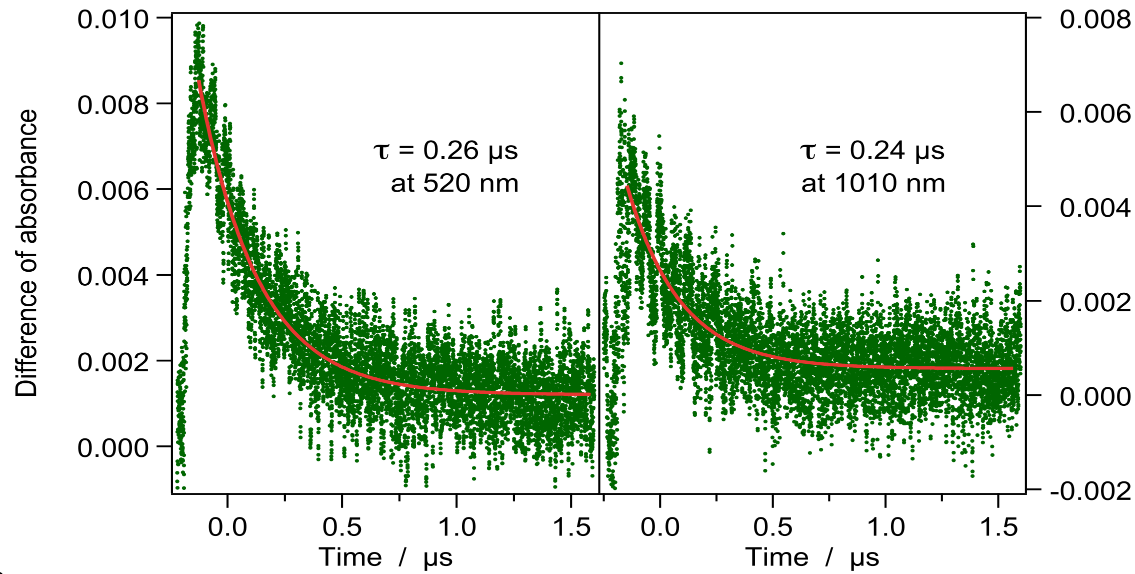
Fullerene-based molecular antennas



τ_{CS} = 260 ns

Dr. A. Kremer

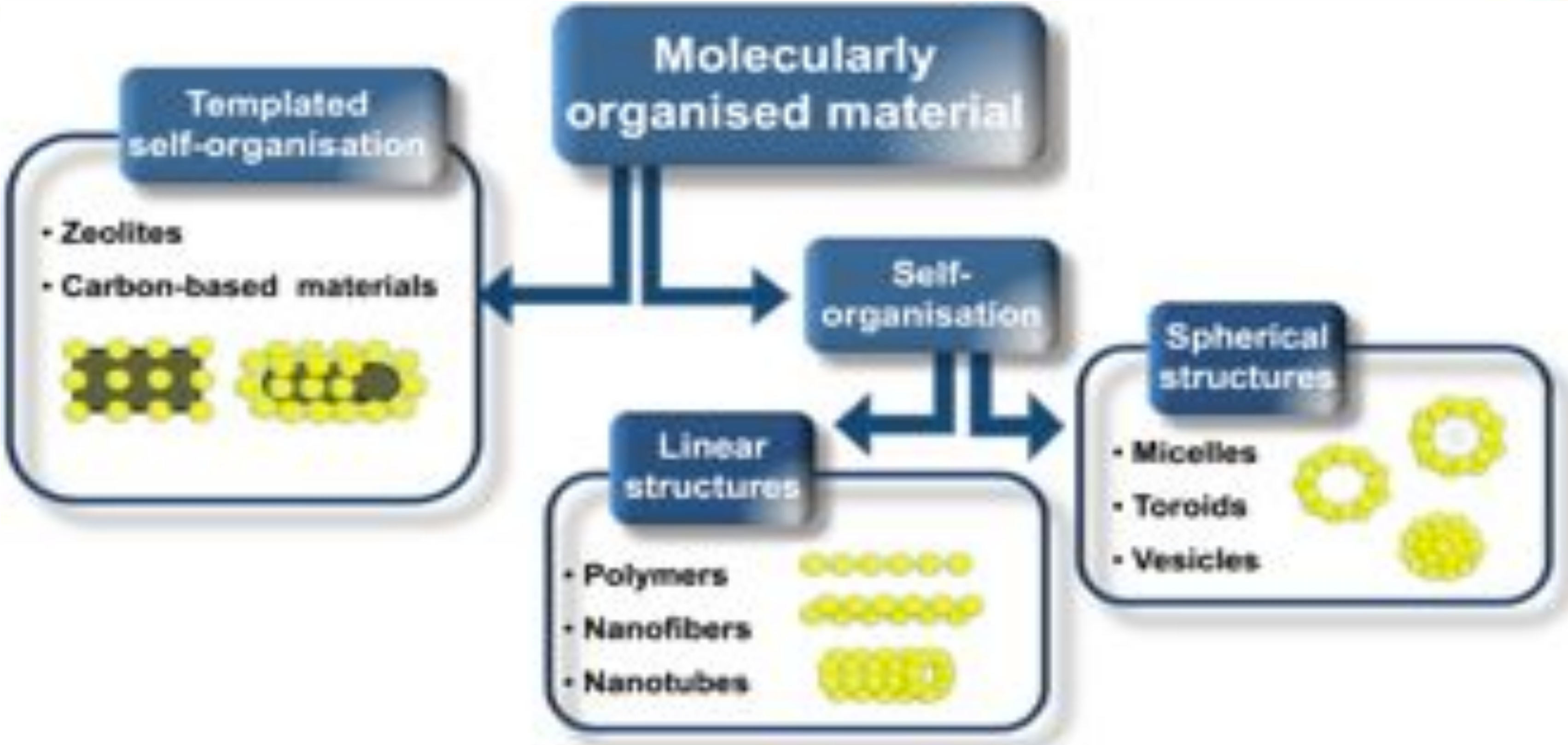




Benzonitrile at 293 K

Unpublished results, in preparation.

Nanostructuring approaches



Non-covalent Interactions

H-Bonding (4-120 kJ/mol)

Metal Coordination (40-120 kJ/mol)

Halogen Bonding (20-40 kJ/mol)

Electrostatic (50-200 kJ/mol)

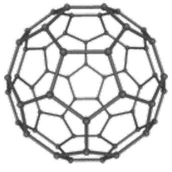
Dipolar Interactions (5-50 kJ/mol)

Pure Appl. Chem. **2010**, *82*, 917; *Chem. Soc. Rev.* **2012**, *41*, 211.

Low-dimensional carbon nanostructures

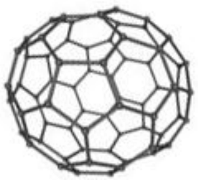
Molecular

C_{60}



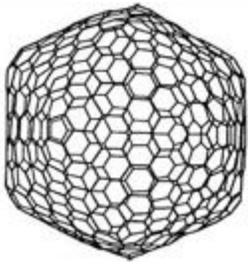
Smalley, R. E. *et al.*
Nature
1985, *318*, 162

C_{70}



Whetten, R. L. *et al.*
J. Phys. Chem.
1990, *94*, 8630

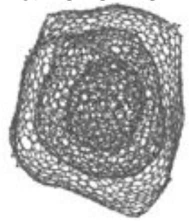
C_{540}



Kroto, H.
Pure Appl. Chem.
1990, *62*, 407

Particellar

Nano-onions

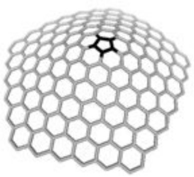


Ugarte, D.
Nature
1992, *359*, 707

Nano-diamond

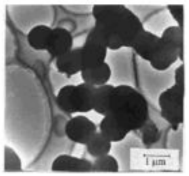
Greiner, N. R. *et al.*
Nature
1990, *343*, 244

Nano-cones



Sattler, K. *et al.*
Chem. Phys. Lett.
1994, *220*, 192

Nano-beads



Zhao, X. L. *et al.*
Carbon
1998, *36*, 507

Nano-horns

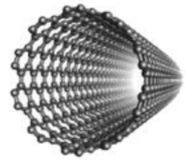
Iijima, S. *et al.*
Chem. Phys. Lett.
2000, *321*, 514

Nano-dots

Scrivens, W. A. *et al.*
J. Am. Chem. Soc.
2004, *126*, 12736

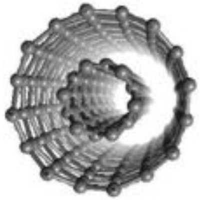
1D

SWCNTs



Ichihashi, T. *et al.*
Nature
1993, *363*, 603

DWCNTs



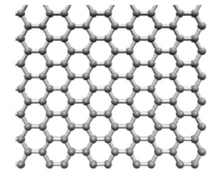
Zakharov, D. N. *et al.*
Carbon
2001, *39*, 761

MWCNTs

Iijima, S.
Nature
1991, *354*, 56

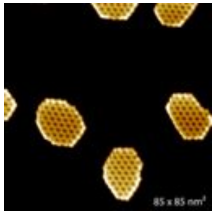
2D

Graphene



Novoselov, K. S. *et al.*
Science
2004, *306*, 666

Graphene nanodots



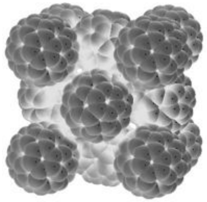
Novoselov, K. S. *et al.*
Science
2008, *320*, 356

Graphene nanoribbons

Dresselhaus, M. S. *et al.*
Phys. Rev. B
1996, *54*, 17954

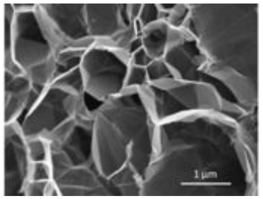
3D

Fullerite



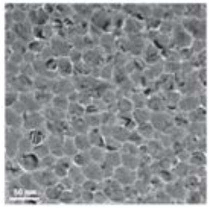
Thiel, F. A. *et al.*
Nature
1991, *351*, 380

Graphene nanoplatelets



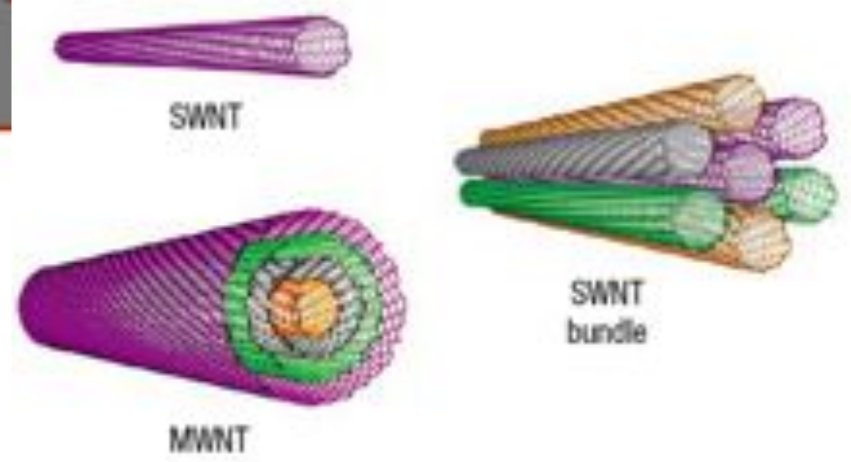
Thiel, F. A. *et al.*
Nature
1991, *351*, 380

Nanocristalline diamond films



Gruen, D. M. *et al.*
Annu. Rev. Mater. Sci.
1999, *29*, 211

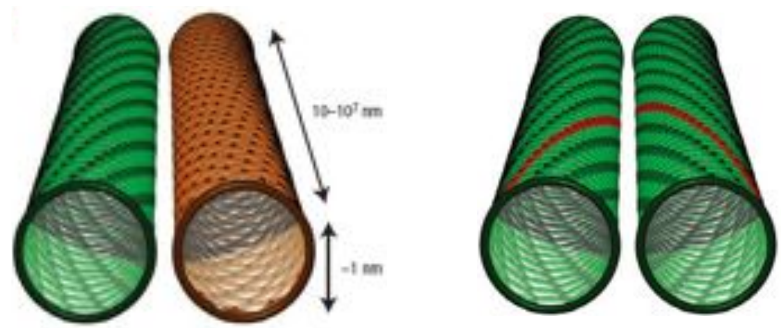
Carbon nanotubes



PROPERTIES

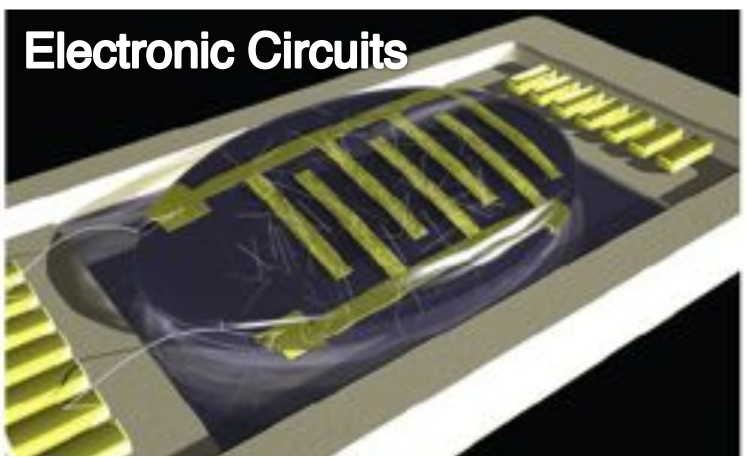
- •**High carrier mobilities** (~1,20,000 $cm^2 V^{-1} s^{-1}$)
- •**Large surface areas** (~1600 $m^2 g^{-1}$)
- •**Absorption in the IR range** (E_g: 0.48 to 1.37 eV)
- •**Conductance** - Independent of the channel length
- •**Great current carrying capability** – 10^9 A cm^{-2}
- •**Semiconducting CNTs –** Ideal solar cells
- •**Mechanical strength & Chemical stability**

Chiral and Achiral SWCNTs   Mirror Images



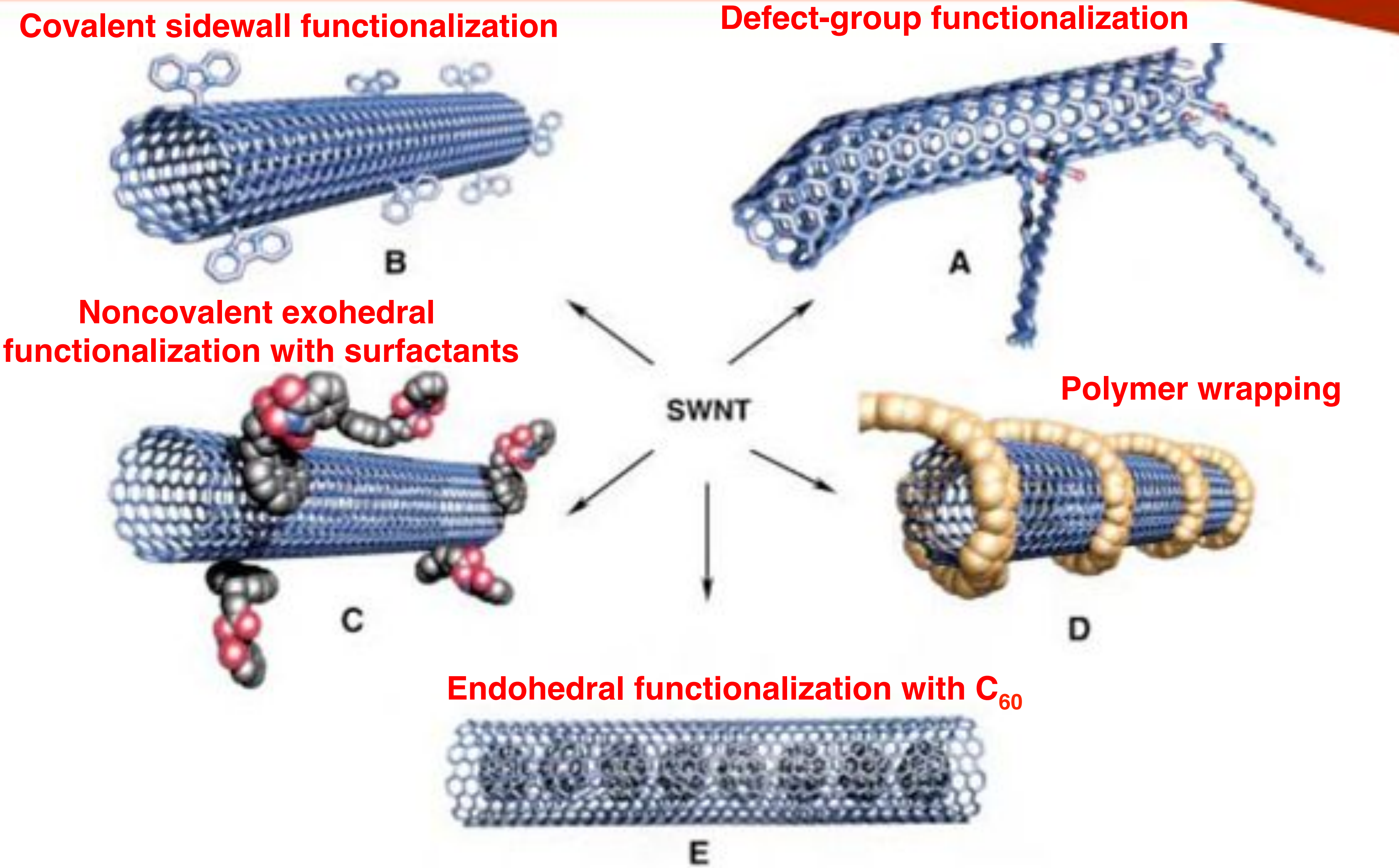
CURRENT DRAWBACKS

- •**Not homogenous structural distribution**
- •**Mixtures of metallic and semiconductor**
- •**Different diameters**



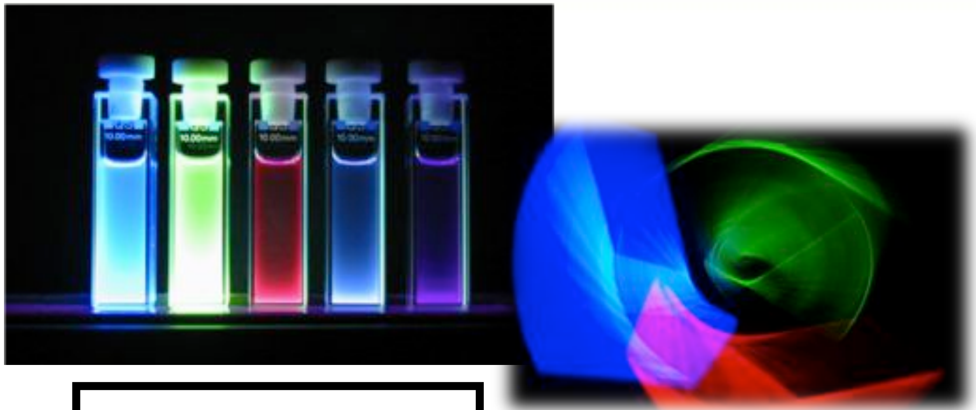
Nature Nanotech. **2008**, 3, 387.

Chemistry of Carbon Nanotubes



(a) Hirsch, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1853; (b) Haddon, R. C. *et al. Acc. Chem. Res.* **2002**, *35*, 1105 (c) Khlobystov A. N. *et al. Acc. Chem. Res.* **2005**, *38*, 901; (d) Prato, M. *et al. Chem. Rev.* **2006**, *106*, 1105; (e) Bonifazi, D. *et al. Chem. Soc. Rev.* **2009**, *38*, 2214.

Creation of new CNT-based luminescent hybrids



Lanthanides

- Intense line-like emission
- Long lifetime decay
- Ease of synthesis/tuning of properties

K. Binnemans, *Chem. Rev.* **2009**, *109*, 4283; S. V. Eliseevaa, J.-C. G. Bunzli, *Chem. Soc. Rev.* **2010**, *39*, 189.

CNTs

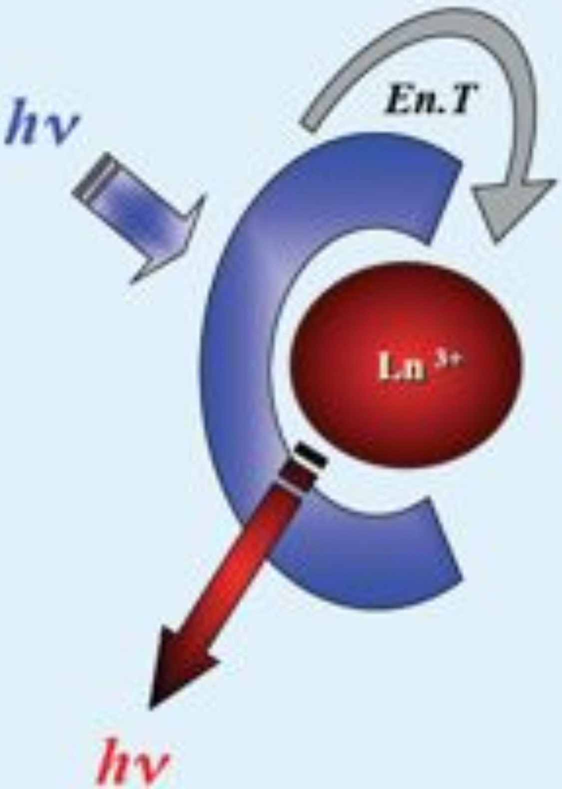
- Conducting or semiconducting properties
- One-dimensional structure
- Several functionalization methodologies available

S. Iijima, *Nature* **1991**, *354*, 56; C. N. R. Rao, B. C. Satishkumar, A. Govindaraj, M. Nath, *ChemPhysChem* **2001**, *2*, 78.

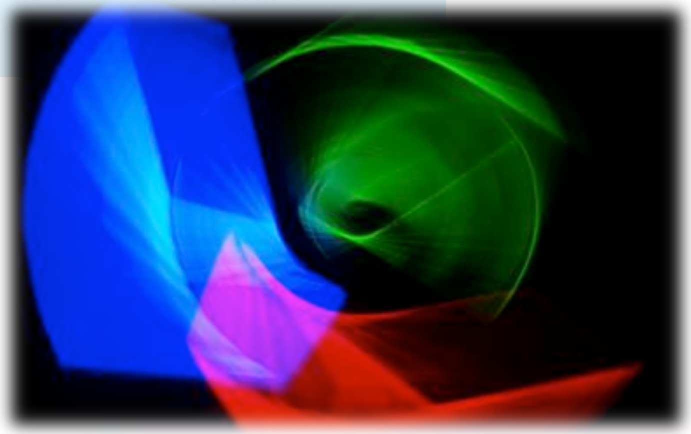
PROBLEMATICS:

- Interchromophoric quenching issues
- Difficulties to preserve structural organization

Rare-hearth complexes

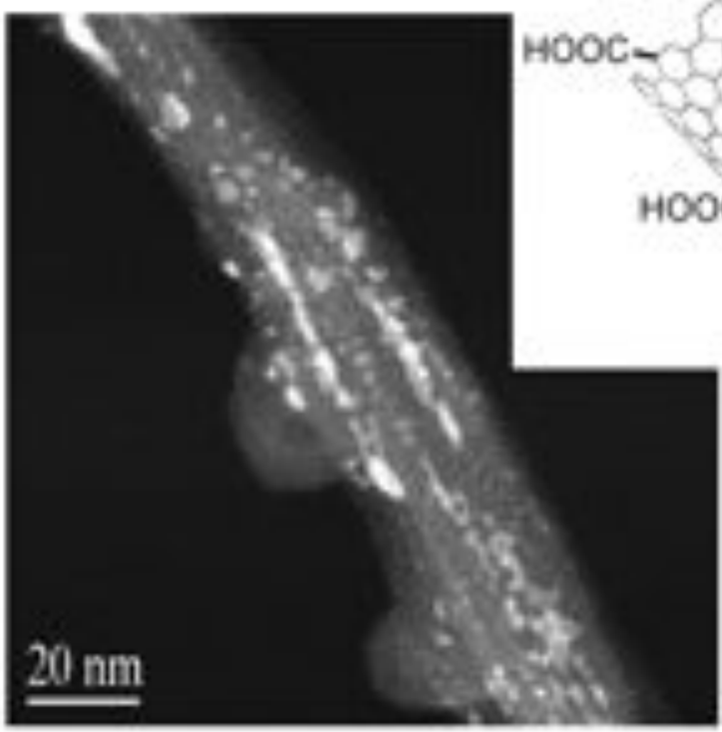


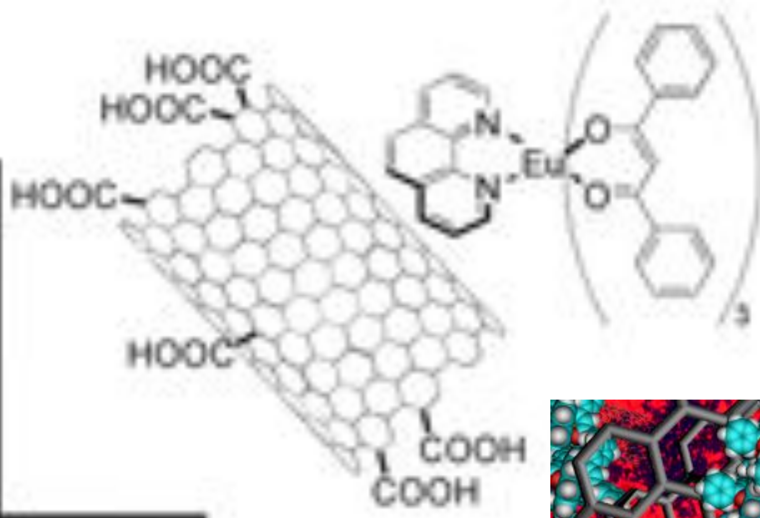
- *Internal transitions (f orbitals)*
- *Intense and line-like emission bands*
- *Long-lived el. excited states (μs-ms)*
- *Broad emission range (Vis-NIR)*
- *PROTECTION OF THE EMITTER BY THE EXTERNAL LIGAND SHELL*

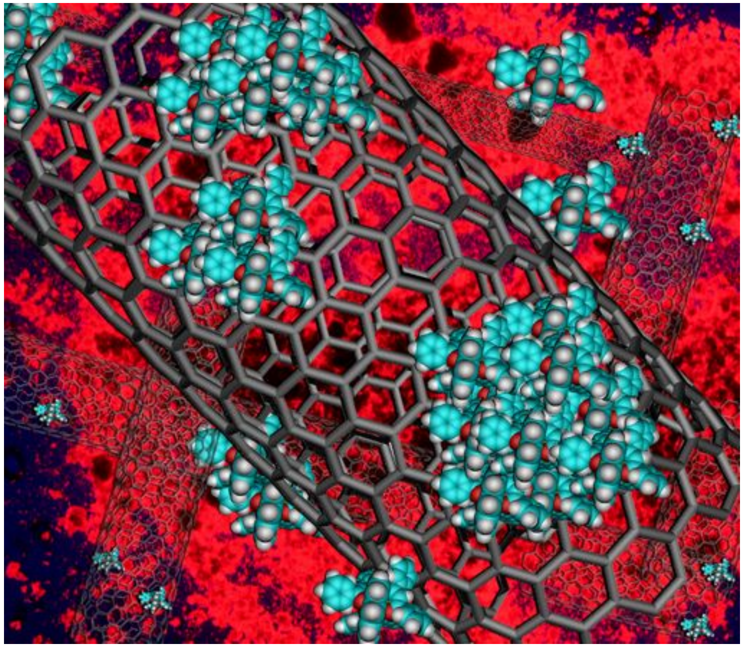


SWCNTs coated with Eu(III) complexes

Z-contrast ADF-STEM micrographs

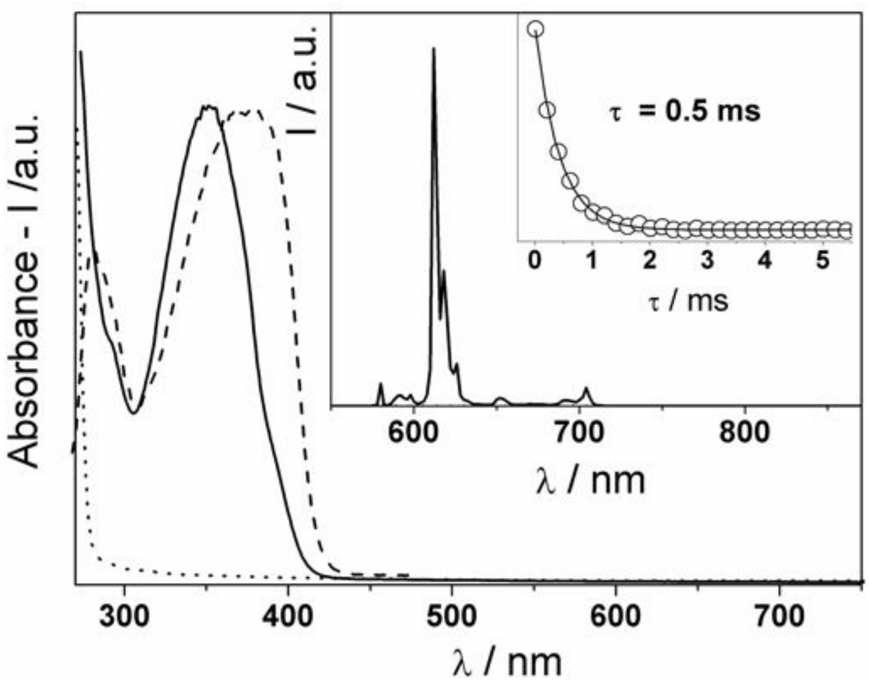




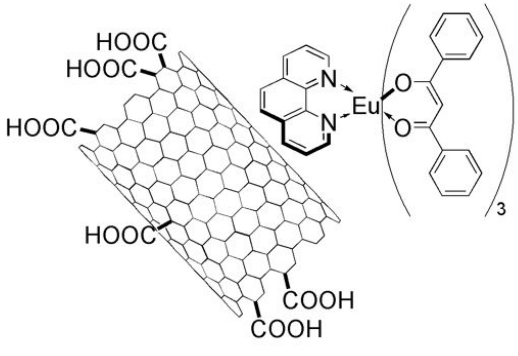


Adv. Funct. Mater., **2007**, *17*, 2975.

Steady-state UV-Vis absorption and emission

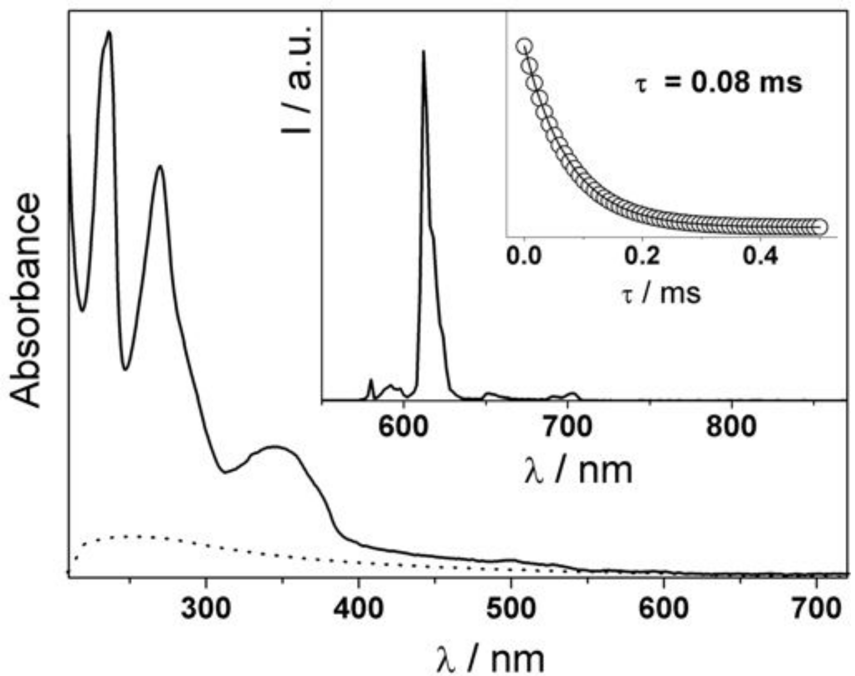


T = 298 K
Matrix: Polyethylene



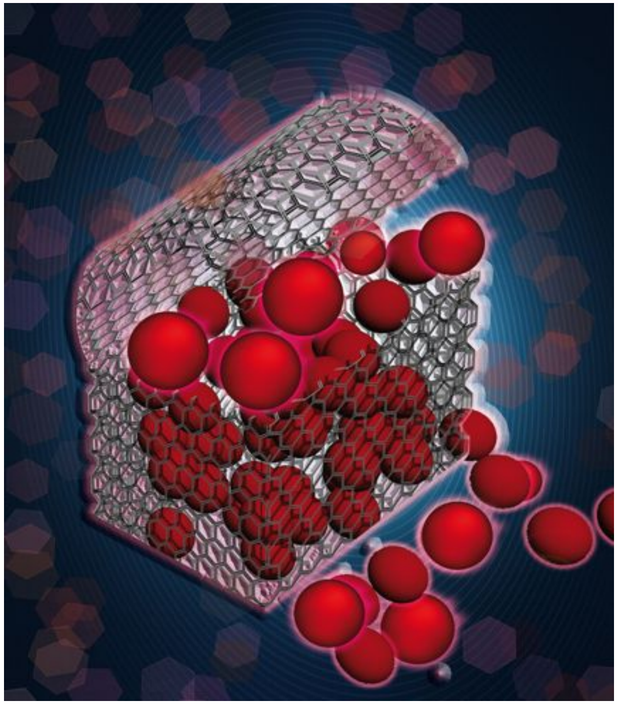
[Eu(Phen)(DBM)$_3$] •SWNT

T = 298 K
MeOH Solution



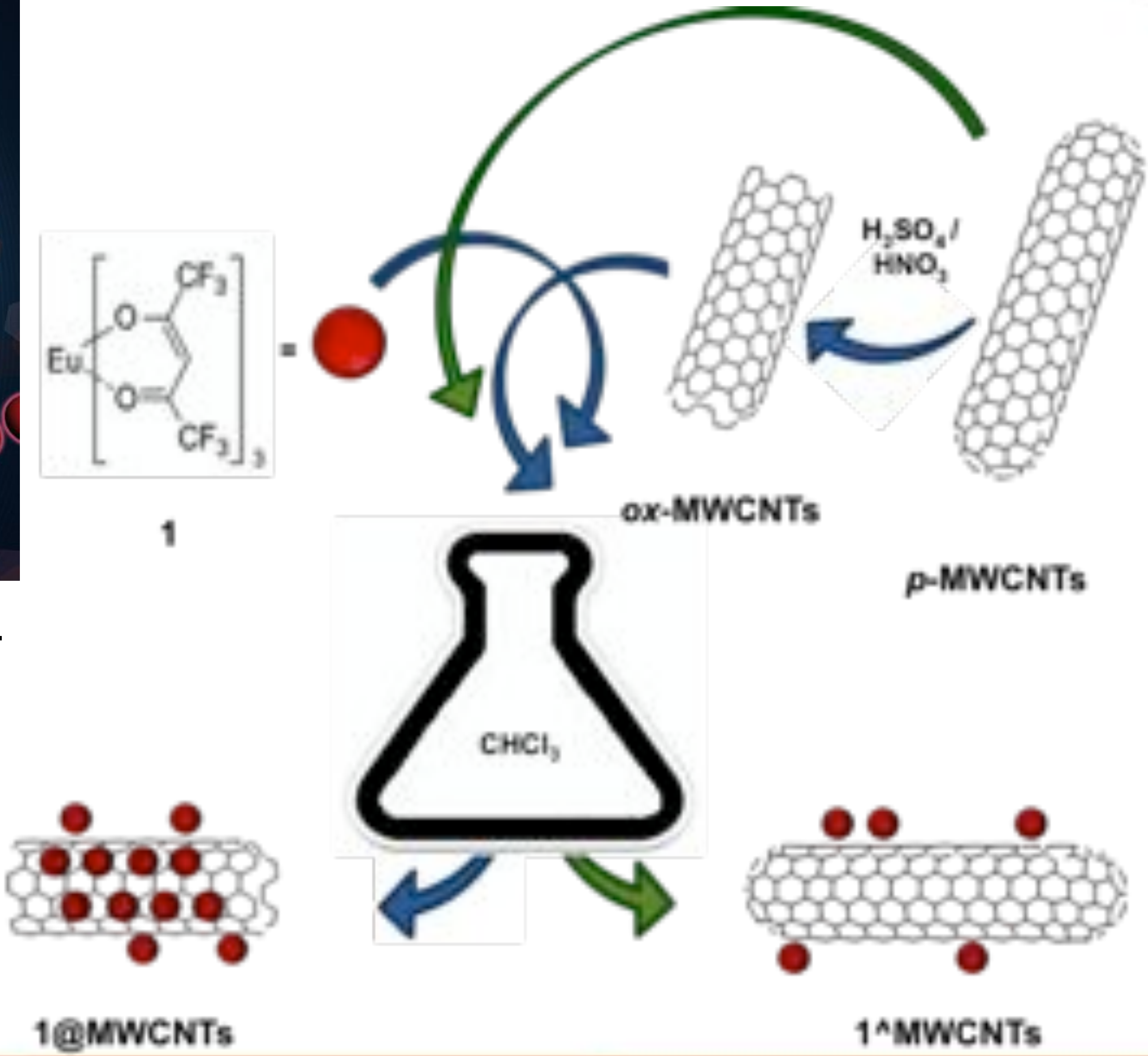
N. Armaroli & G. Accorsi

Luminescent CNTs-Eu(III) host-guest complexes

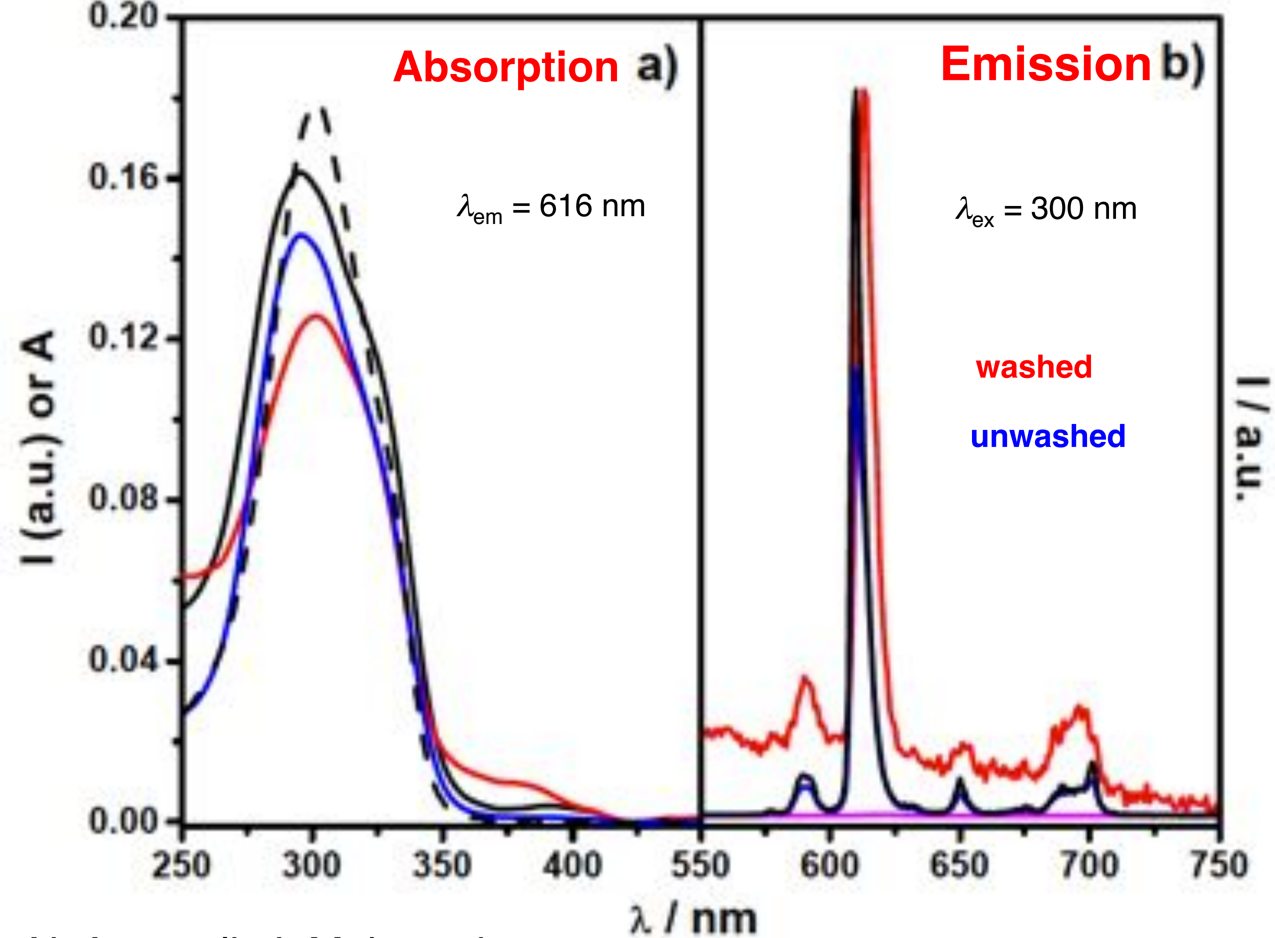


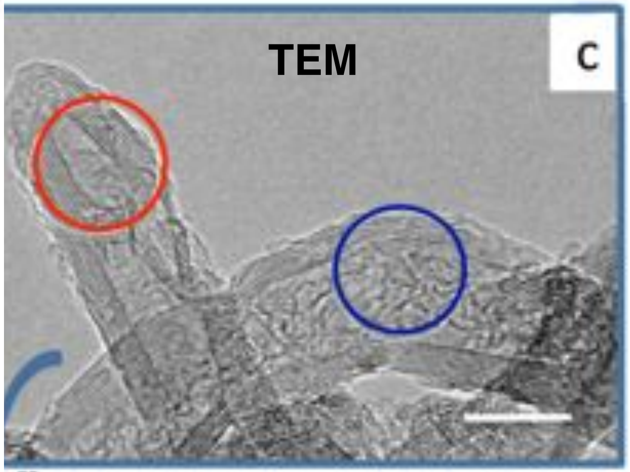
Chem. Eur. J. **2011**, *17*, 8533.

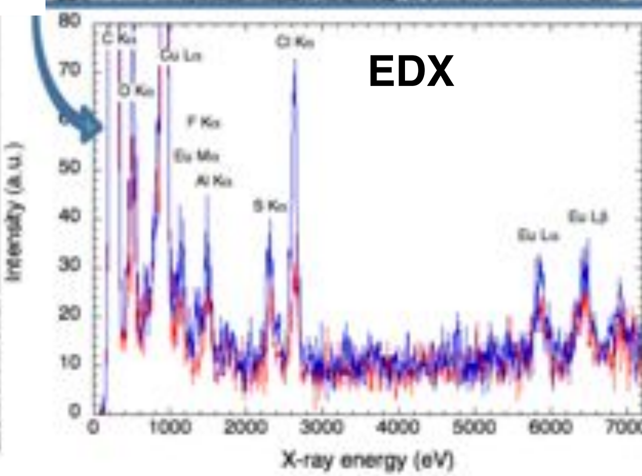
Dr. L. Maggini



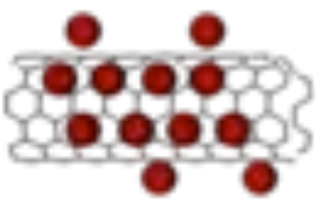
Structural and Photophysical Characterization (Emission and TEM)



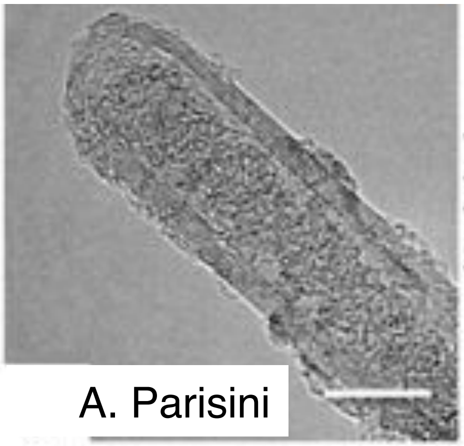




N. Armaroli, J. Mohanraj



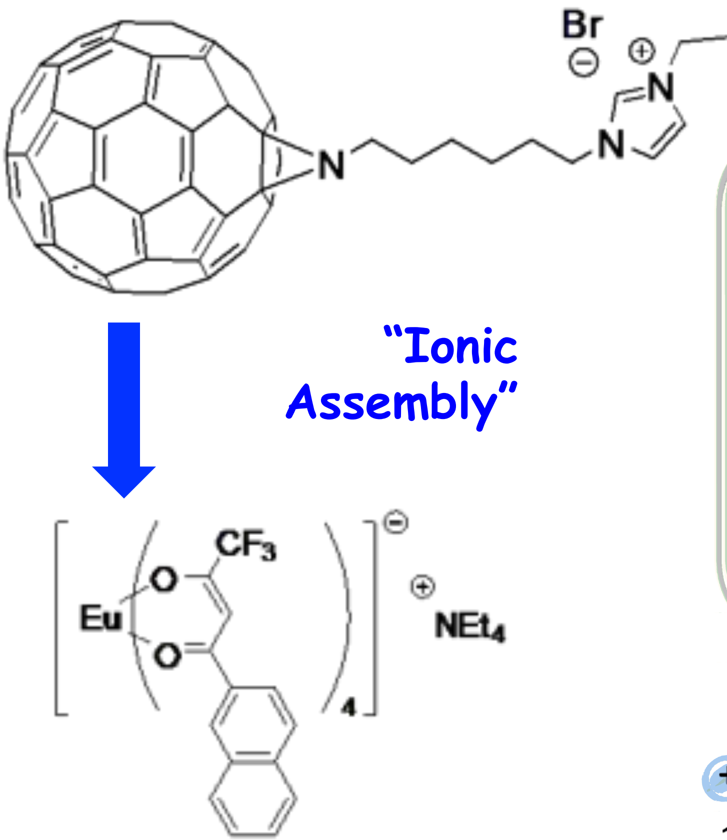
1@MWCNTs



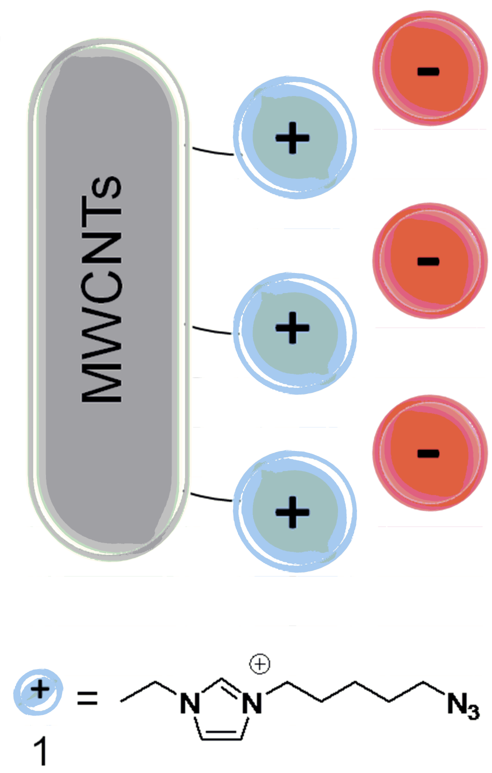
A. Parisini

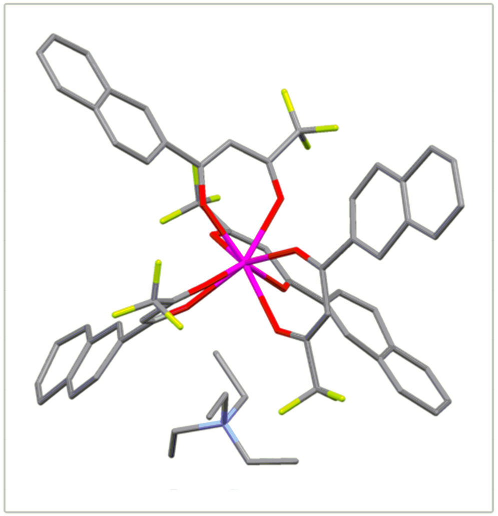
Non-covalent decoration of MWCNTs through ion-pairing interactions

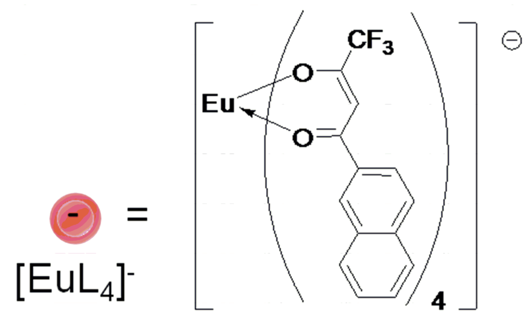
STRATEGY: exploit the columbic interactions between ionic liquids and negatively-charged Lanthanide complexes



Europium complexes designed and synthesized by the group of **Prof. M. Pietraszkiewicz**

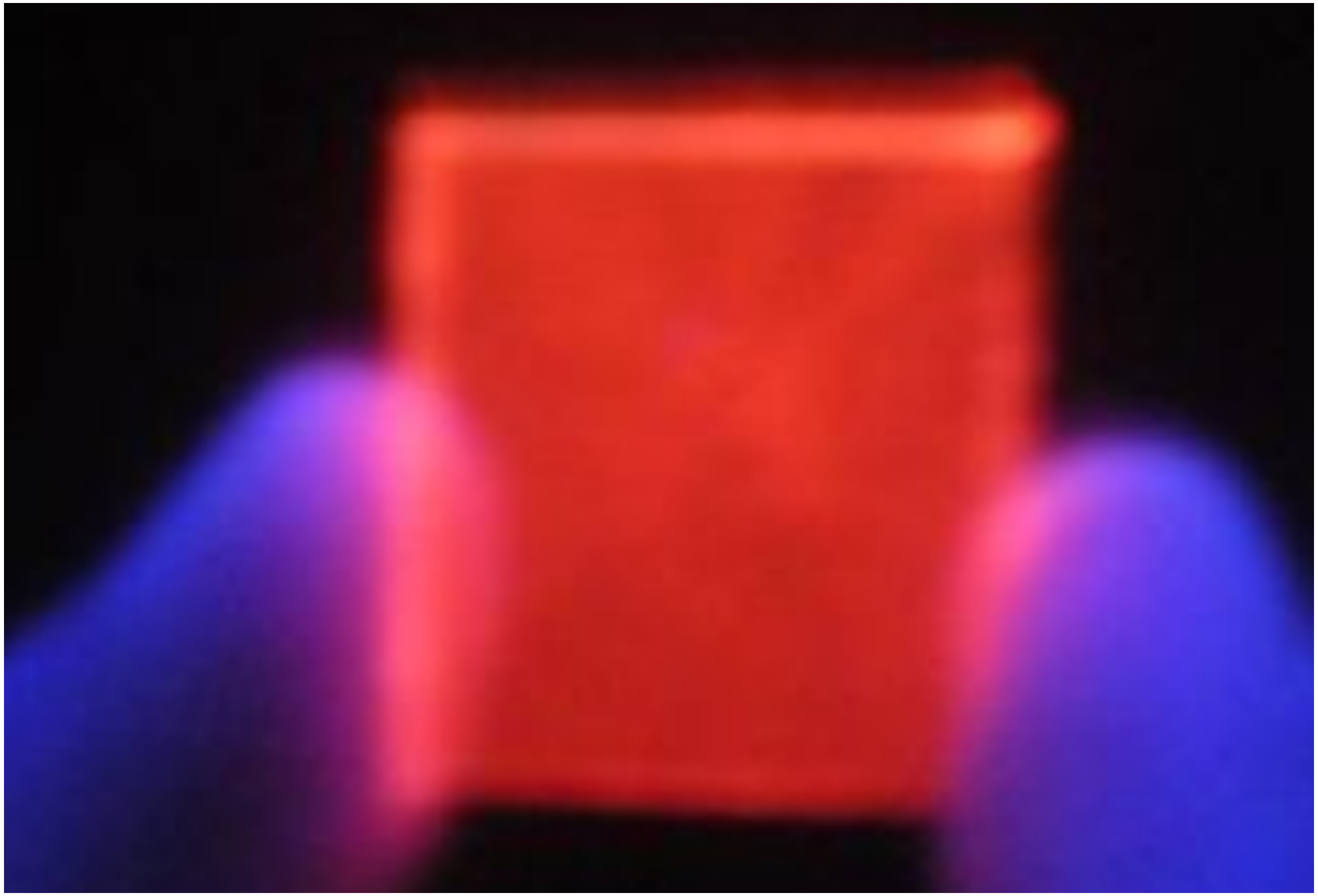






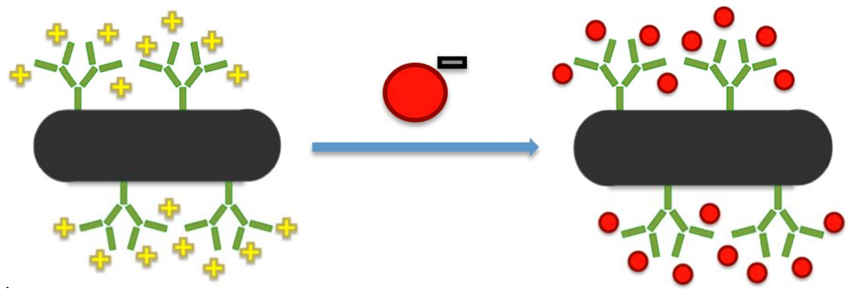
Chem. Commun., **2011**, *47*, 1626

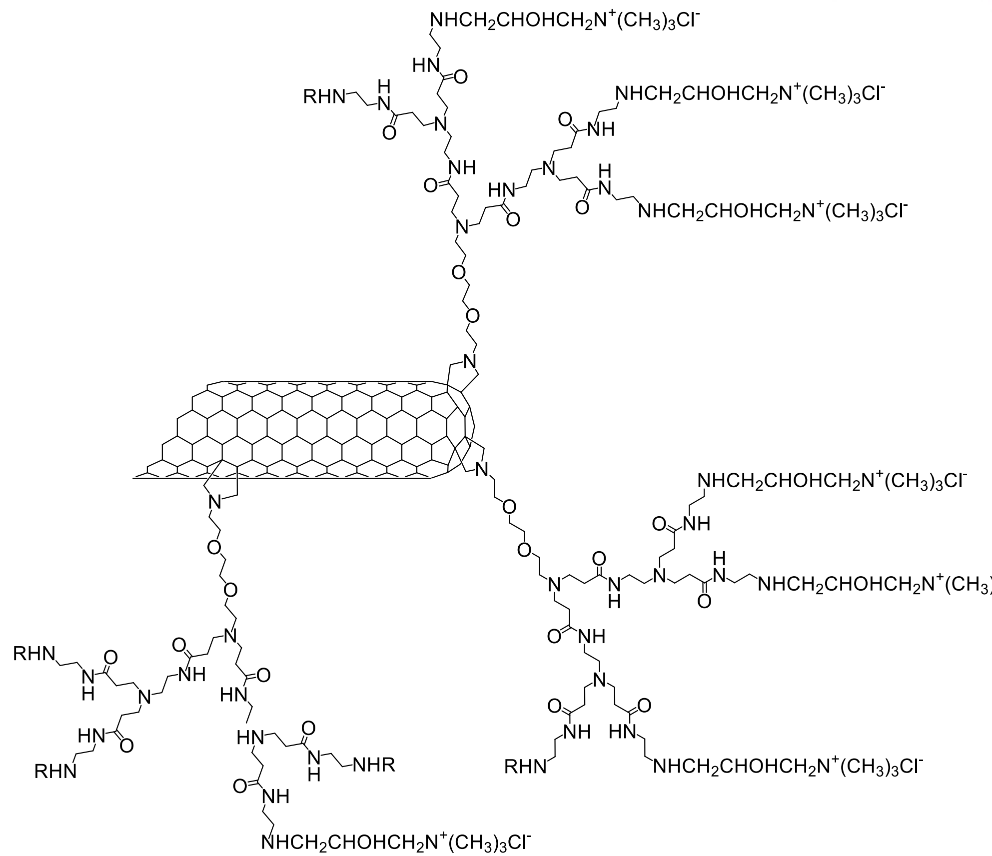
Luminescent materials



Dendronic ion-paired MWCNTs-Eu(III) hybrids

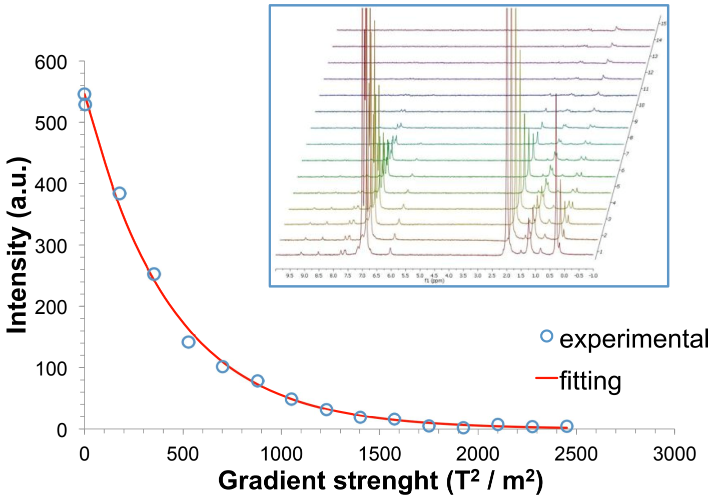
Chem. Eur. J. **2012**, *19*, 5889.



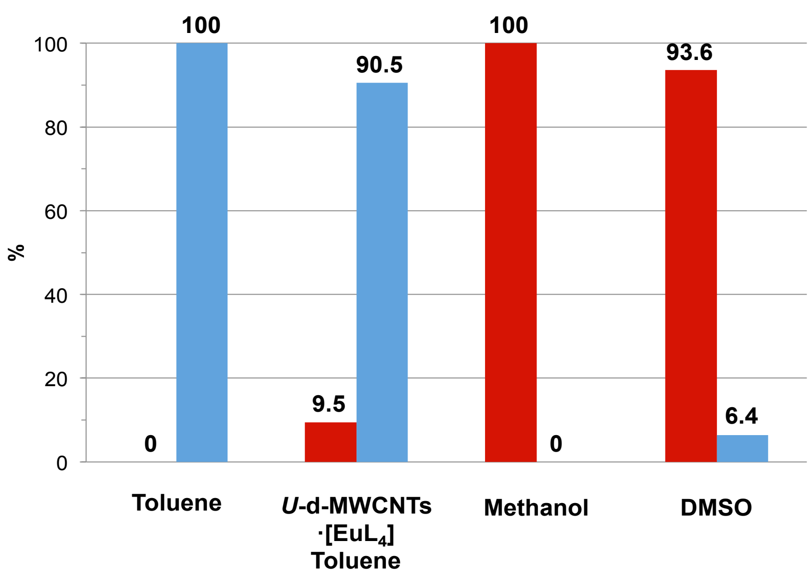


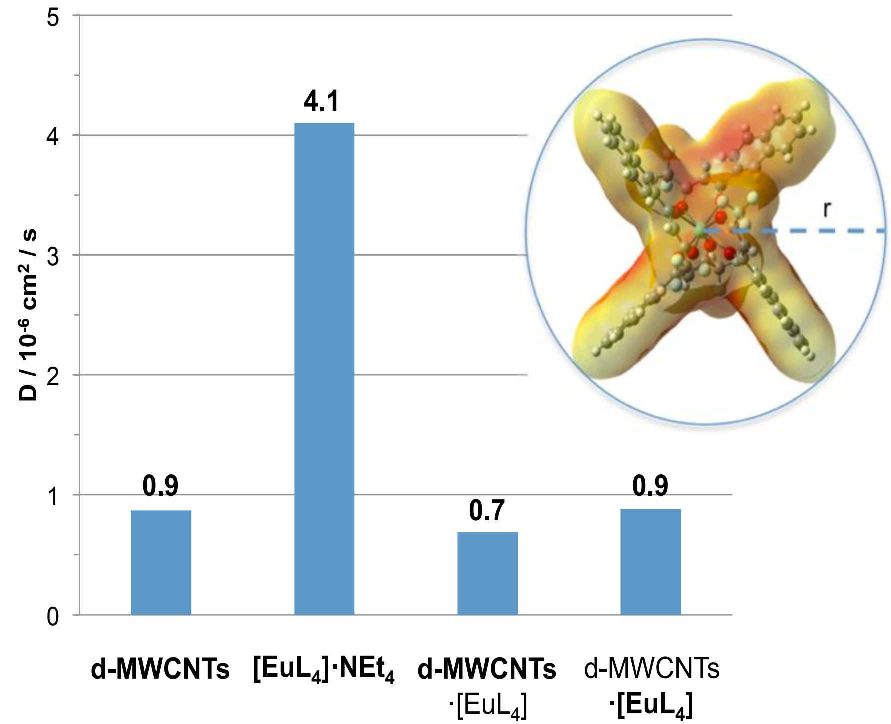
In coll. with M. Prato

DOSY-NMR: effectiveness of the ion-pairing



Free [EuL_4] and d-MWCNTs·[EuL_4]





The DOSY eq.

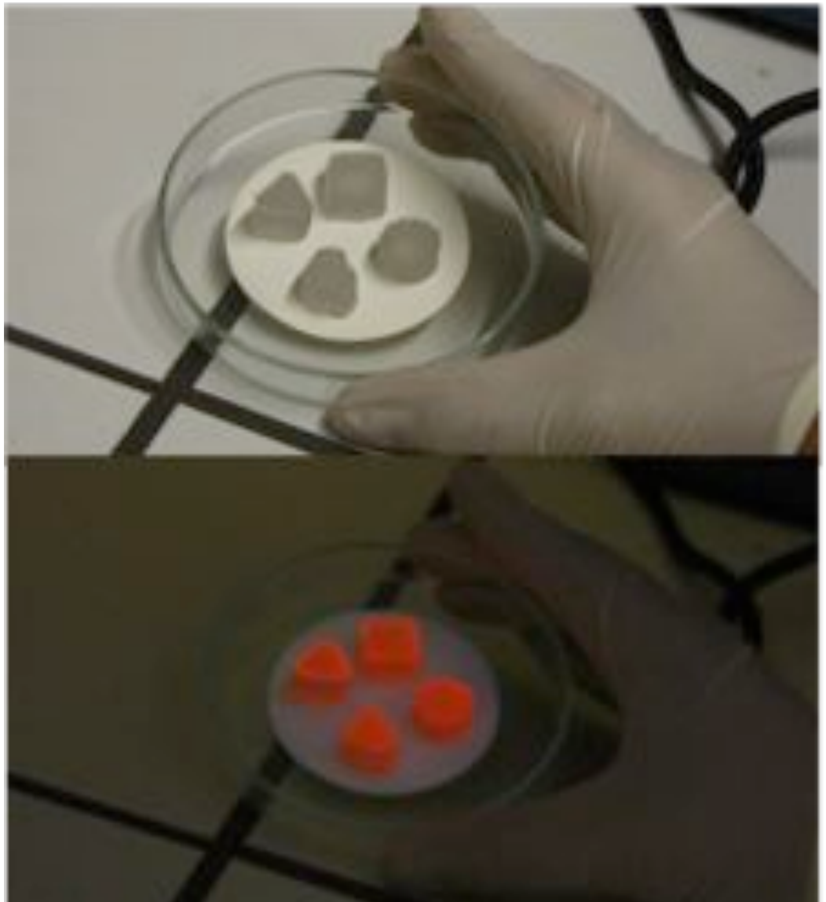
$$I = I_0 \exp(-\mathbf{D} \times \Delta q)$$

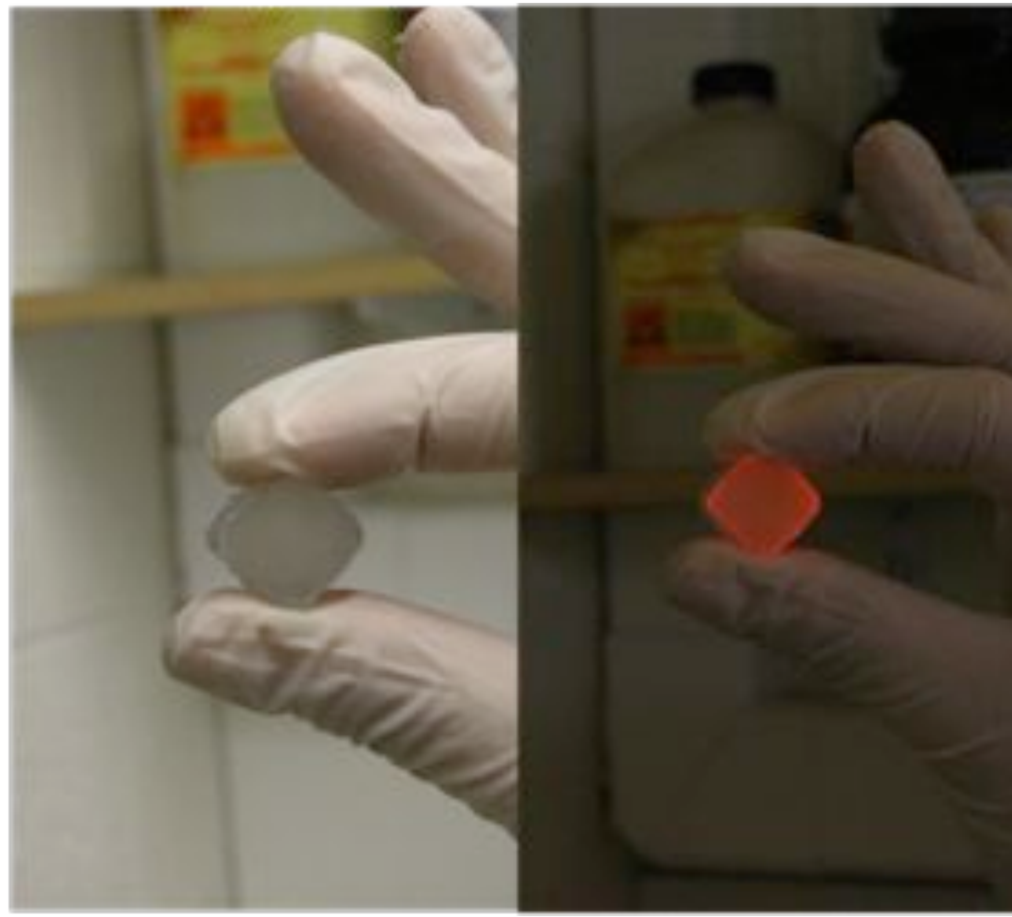
Stokes–Einstein eq.

$$\mathbf{D} = (k_B \times T) / (4 \times \pi \times \eta \times \mathbf{r})$$

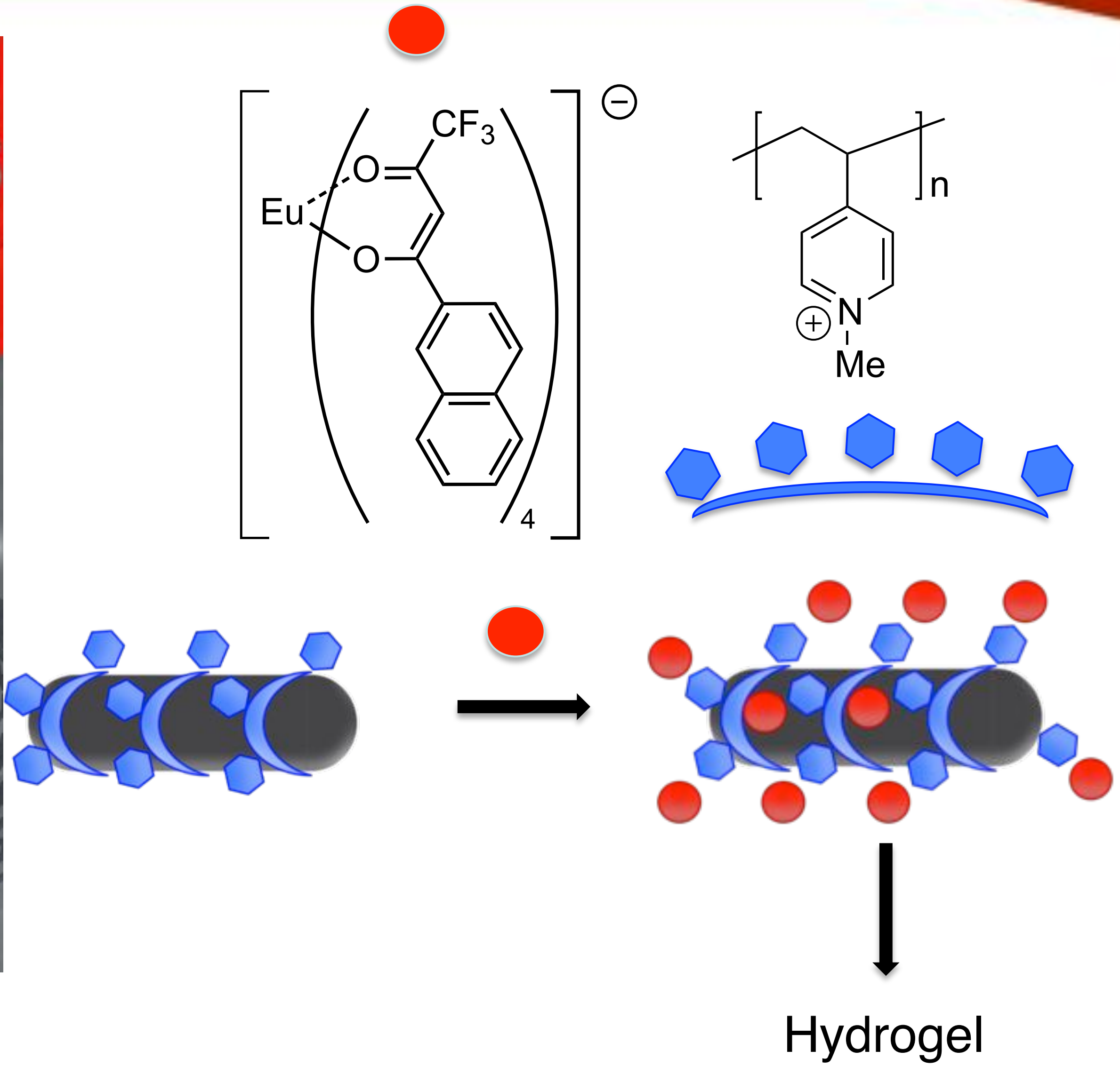
$\mathbf{r_{cal}}$ & $\mathbf{r_{exp}}$: 1.2 & 1.3 nm for **free [EuL_4]**
$\mathbf{r_{exp}}$: 5.7 nm for **d-MWCNTs·[EuL_4]**

Dispersion in polymers



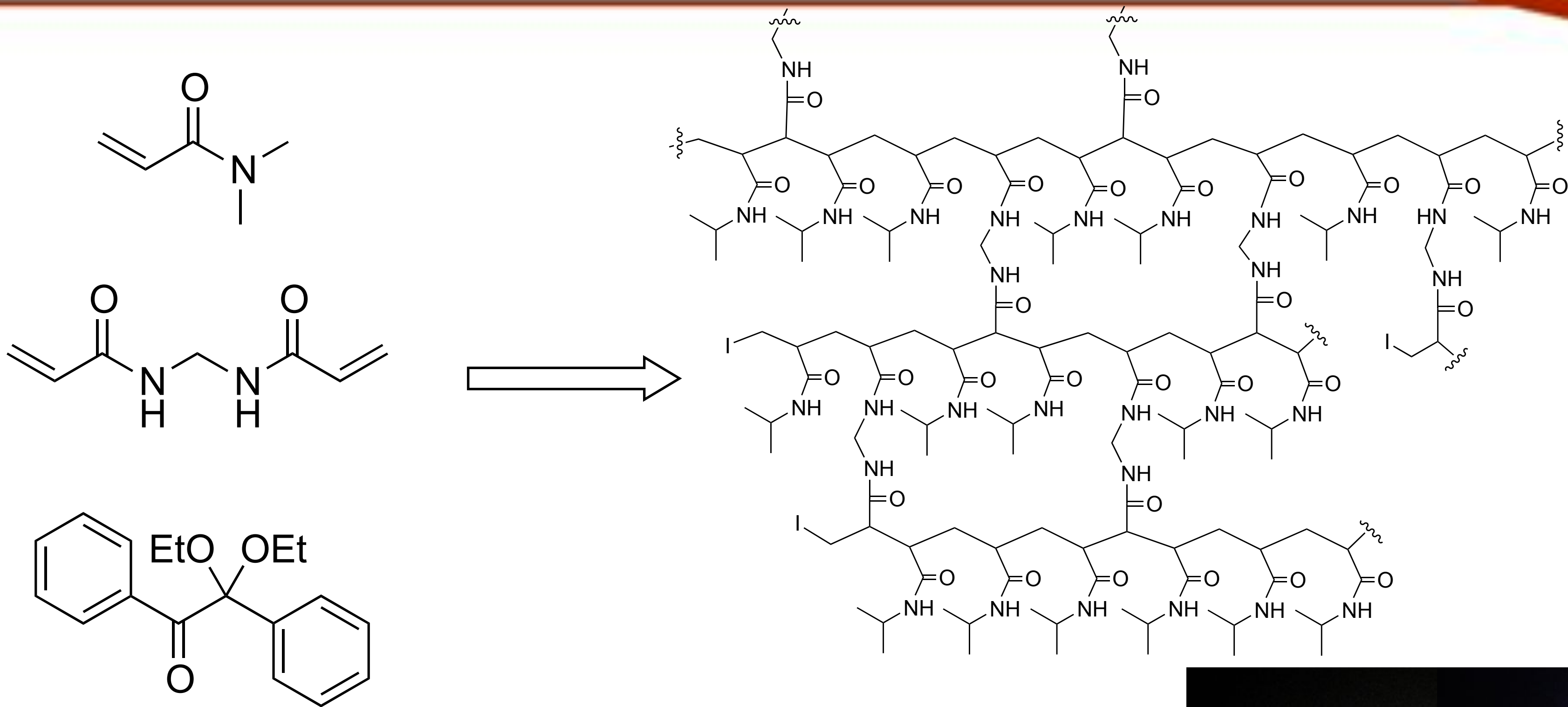


Towards functional materials: CNT-hydrogels



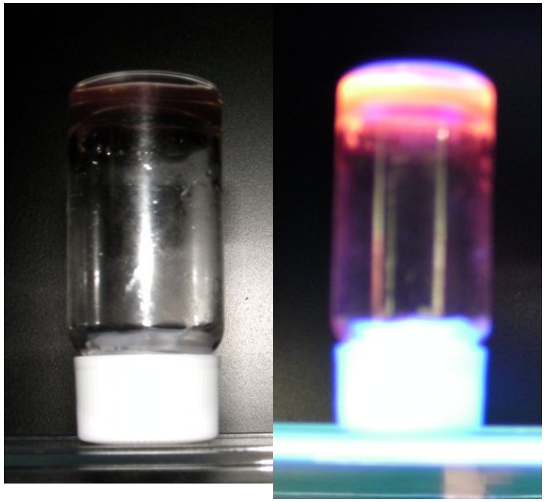
Adv. Mater. **2013**, *25*, 2462.

Hydrogels: preparation



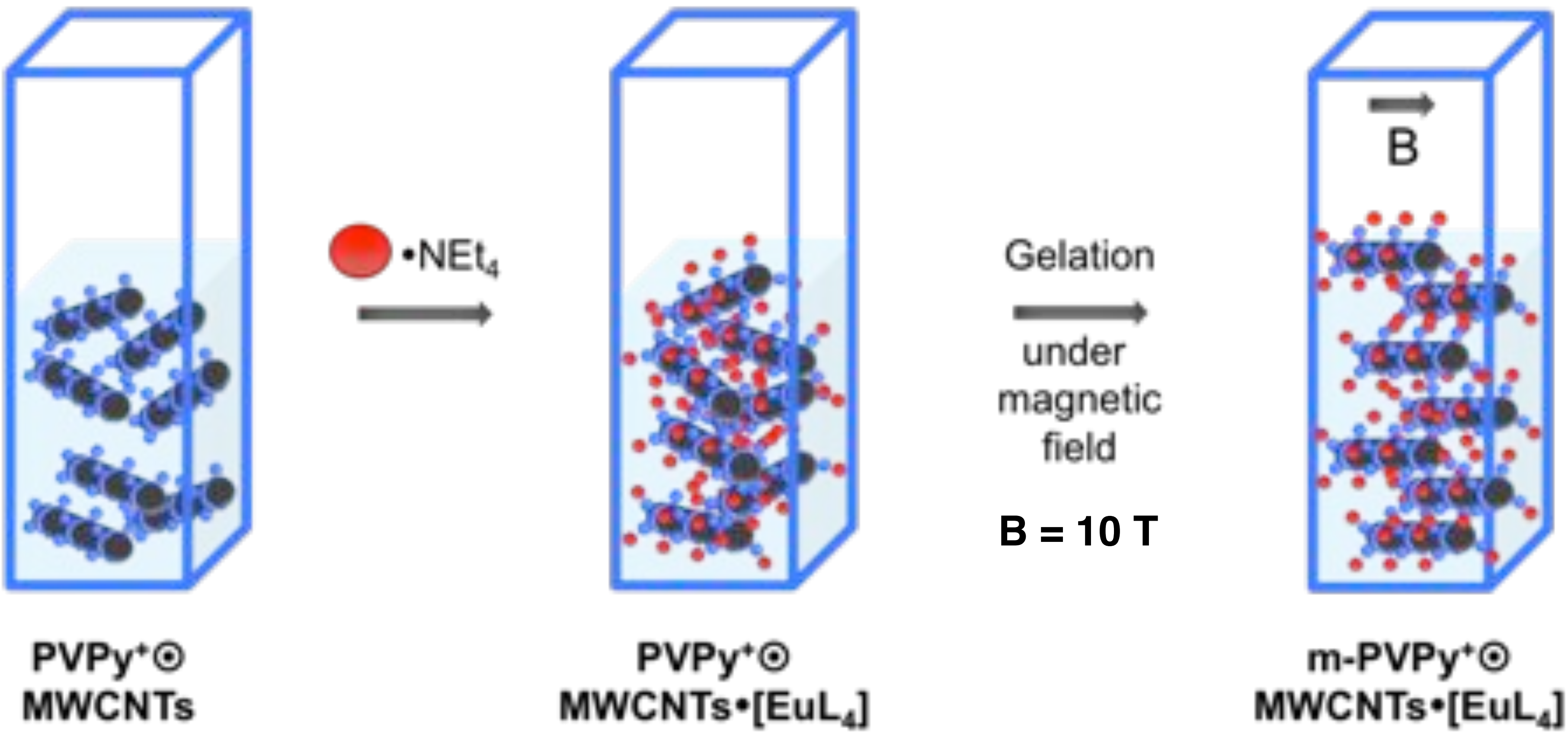
1:2:3 = 100:1:1

- Addition of the complex to the suspension of CNTs
- Addition of the gelators followed by sonication (1 min)
- Irradiation (20 min)

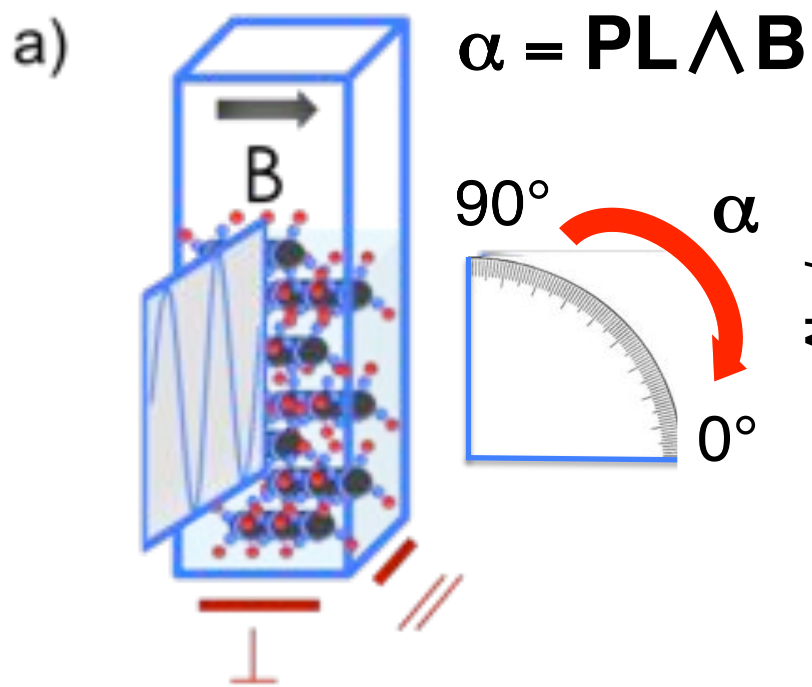


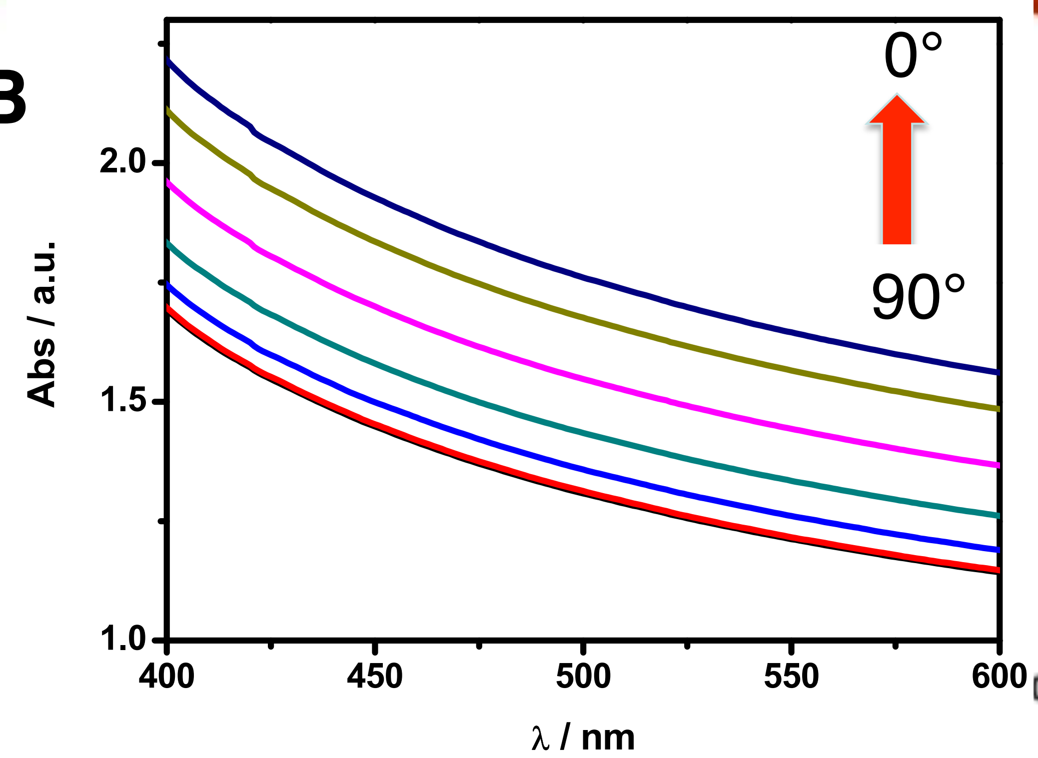
Dr. I. Ishida (Riken Institute, Japan)

Anisotropic luminescent hydrogels: CNT templates

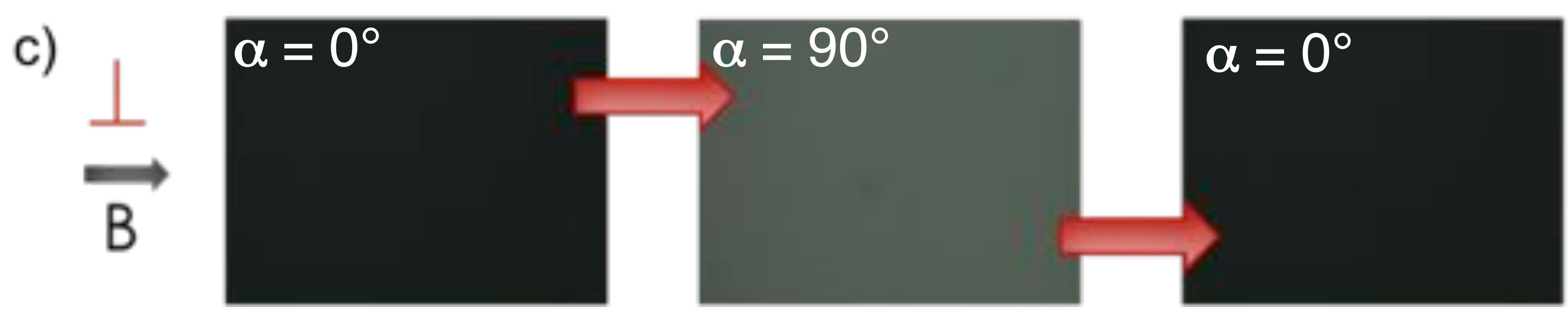


Polarized UV-Vis adsorption

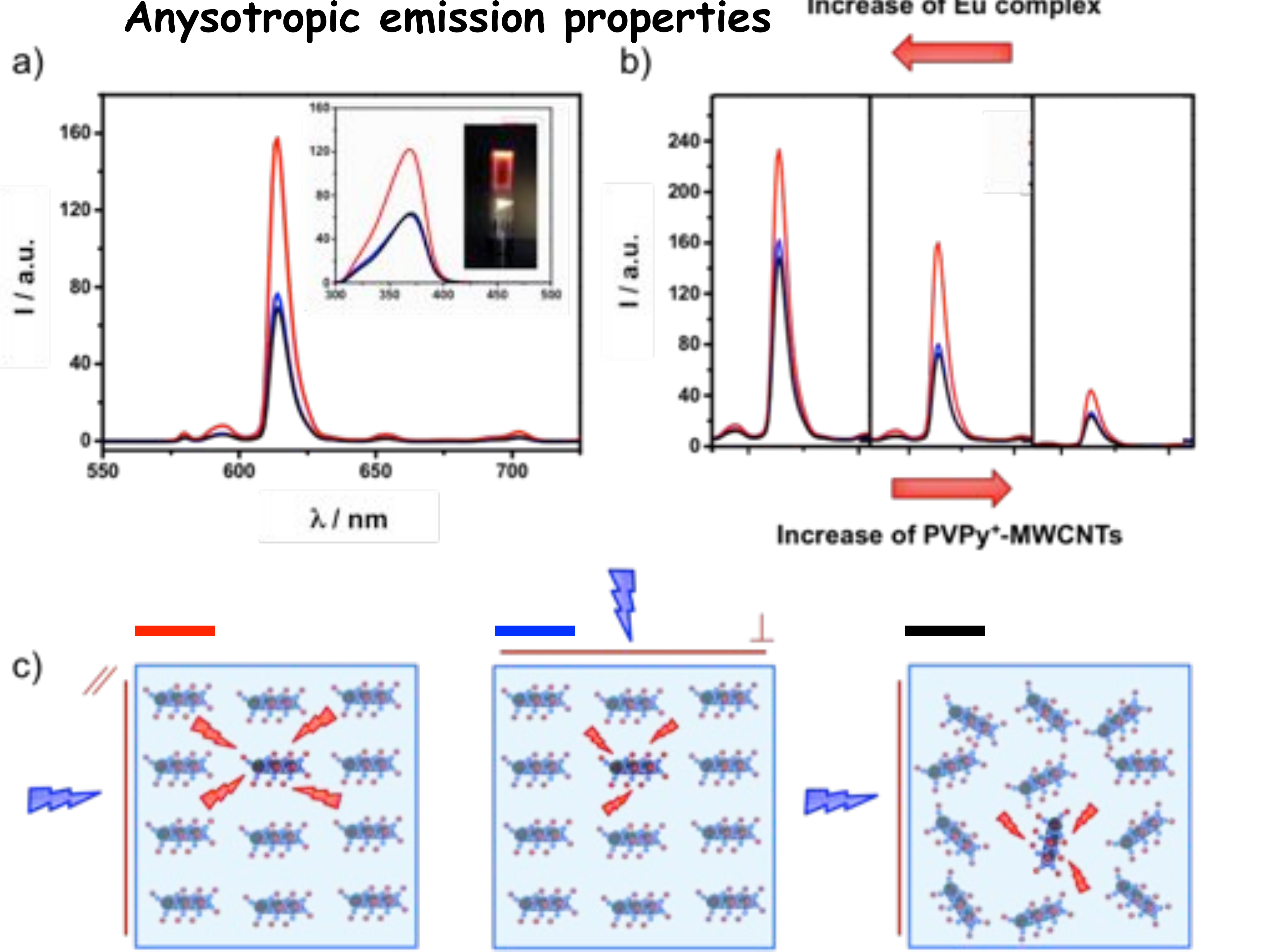


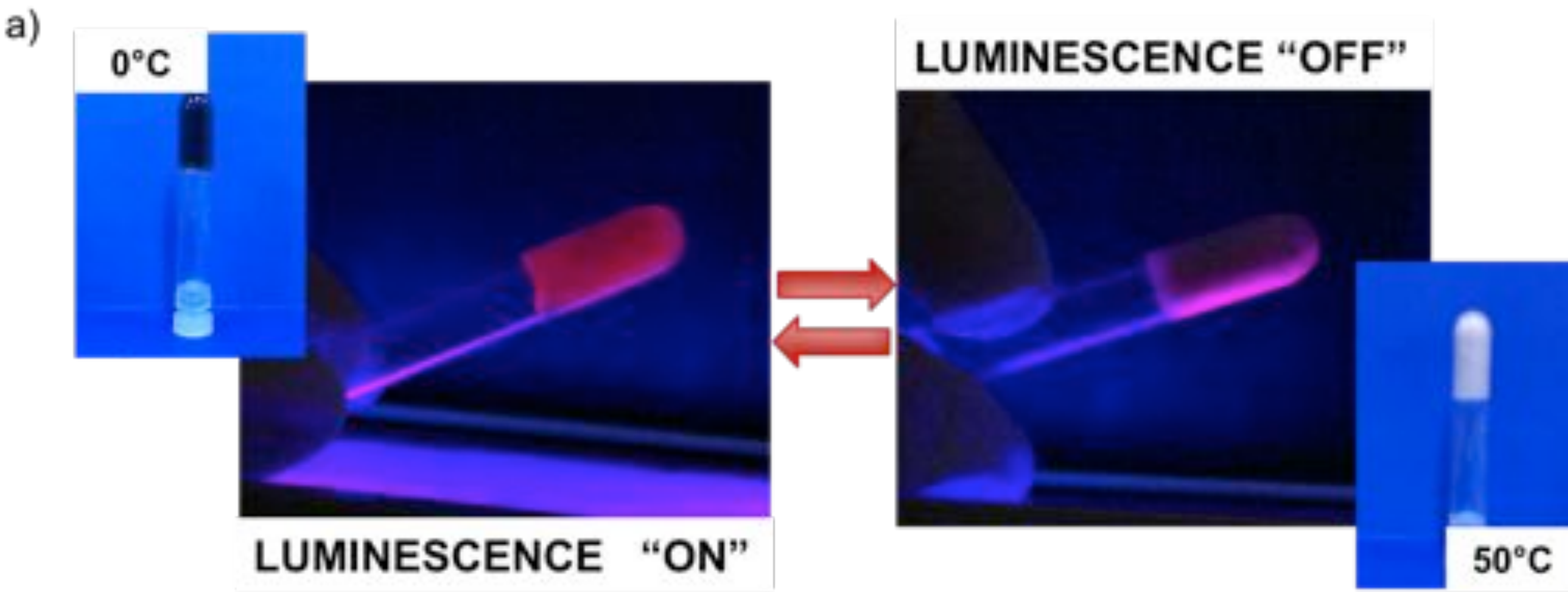


Polarised microscope images

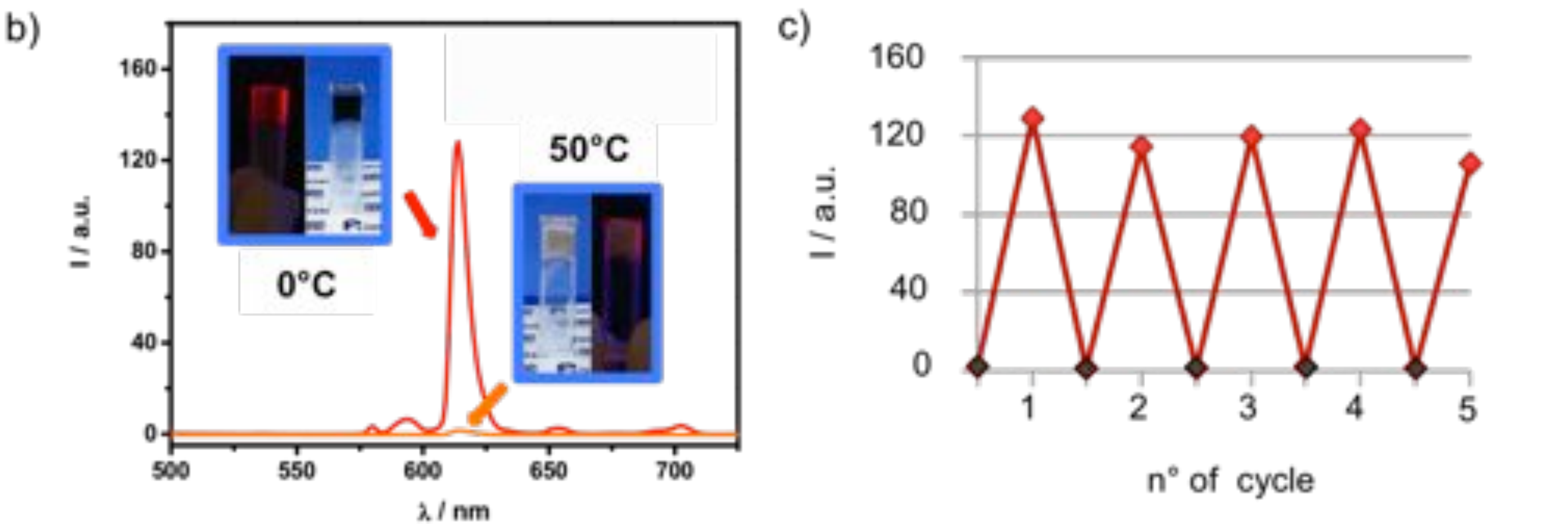


Anysotropic emission properties





Low critical solution temperature (LCST at 33 °C)



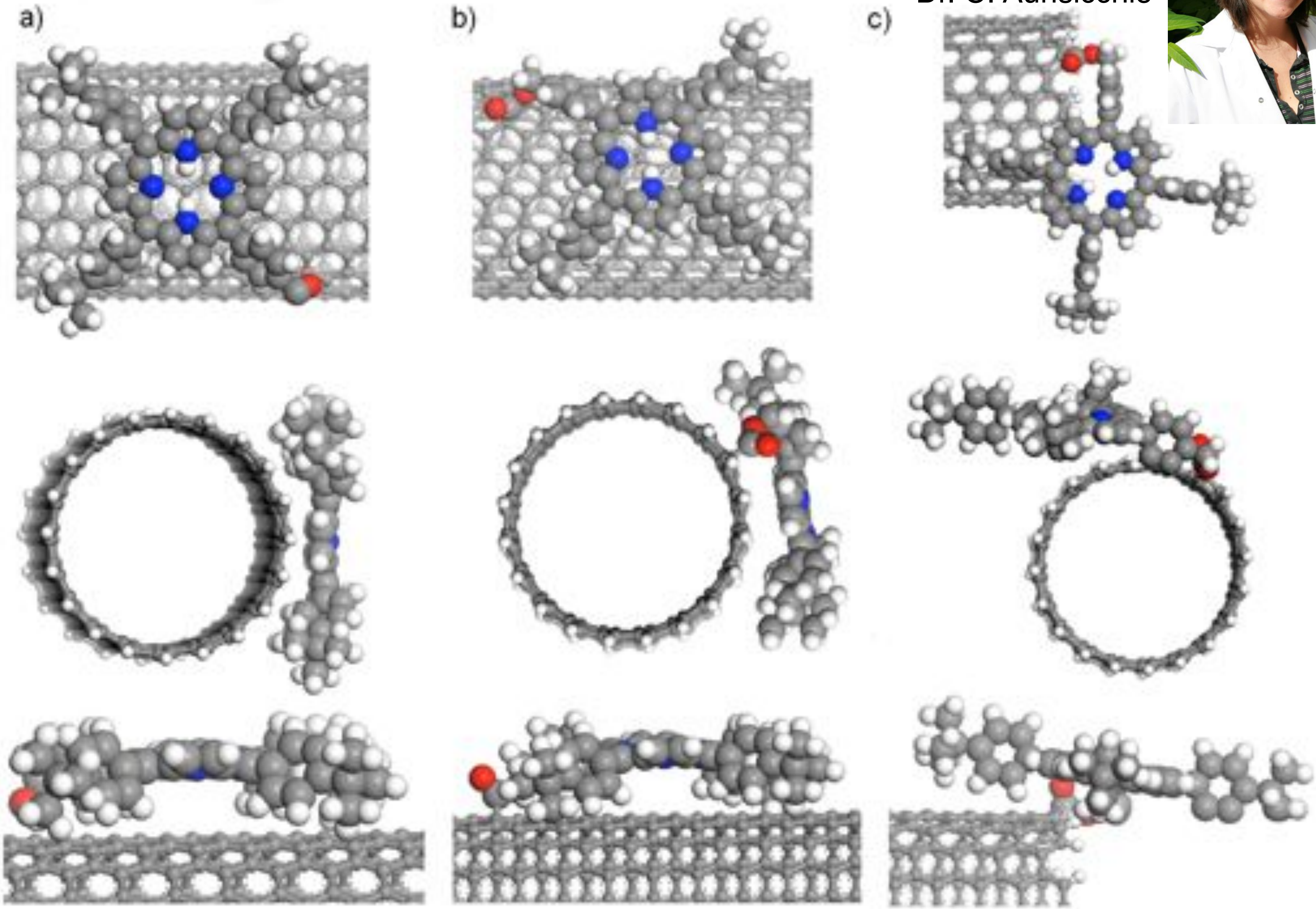
Thermoresponsive luminescent hydrogels

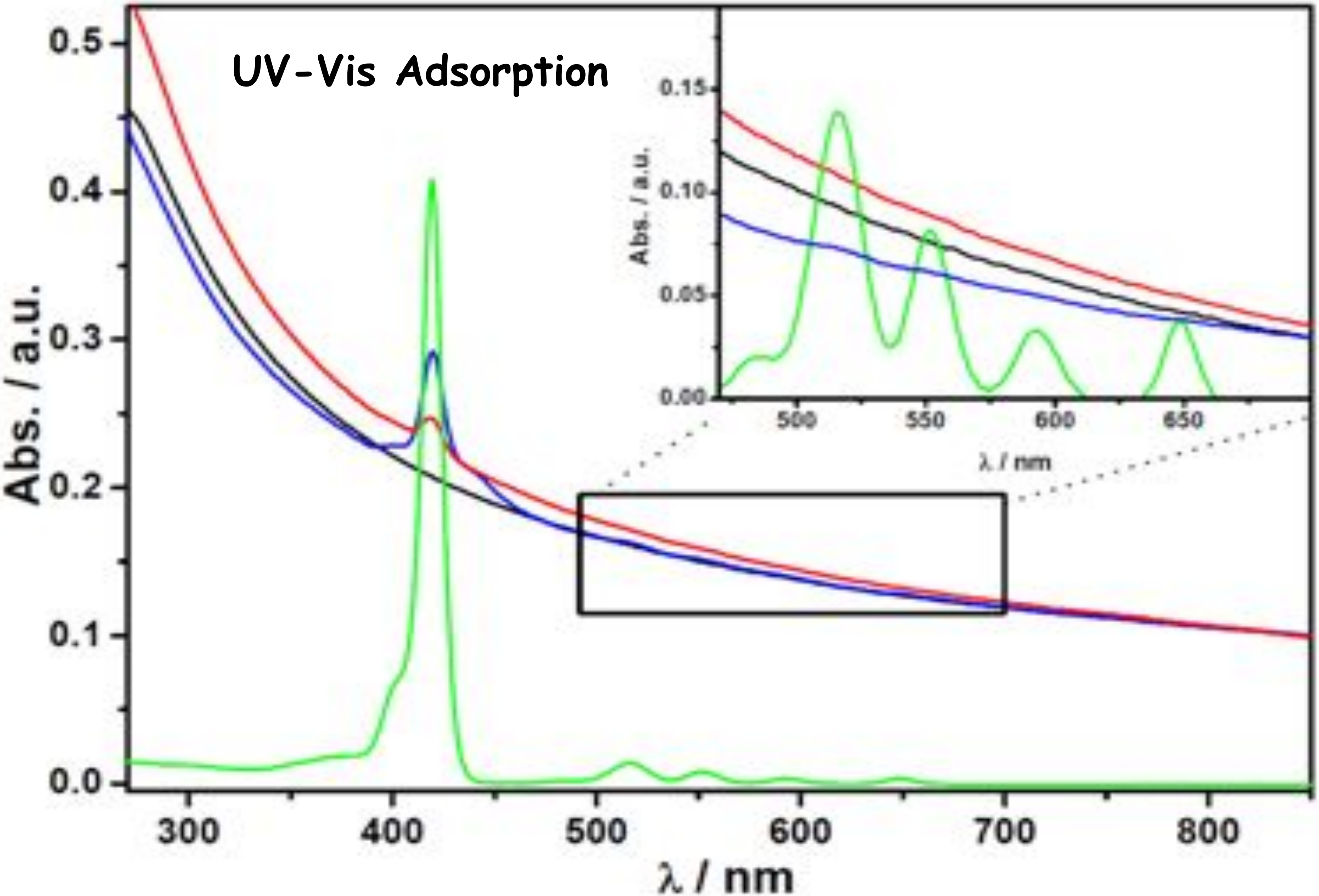
UV-images thin films (height 1 mm) + second polymerisation of NIPAM on the thin film (total height ≈ 2 mm)

Computational Modelling

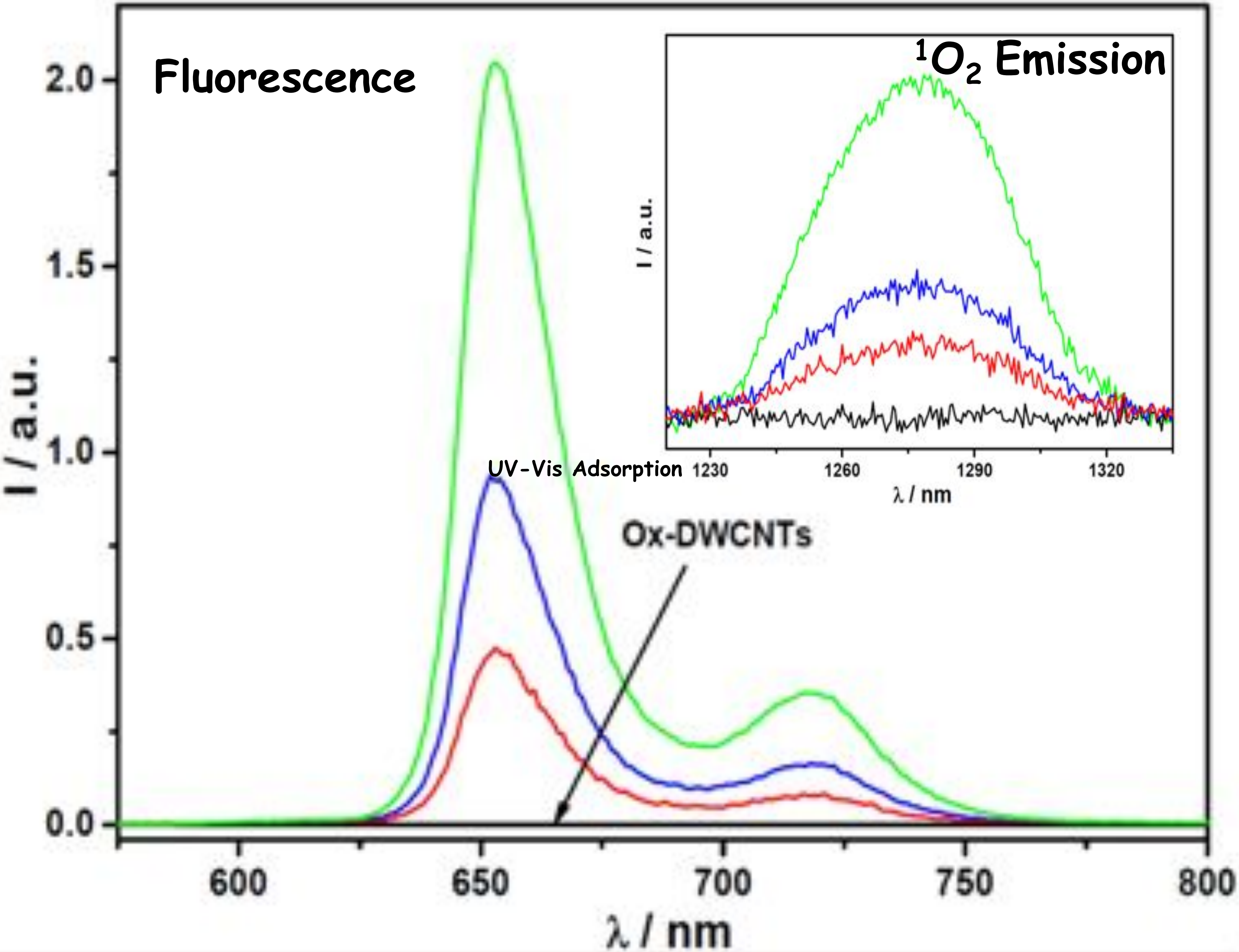
(software: Material Studio 5.0 with Dreiding force field)

Dr. C. Aurisicchio

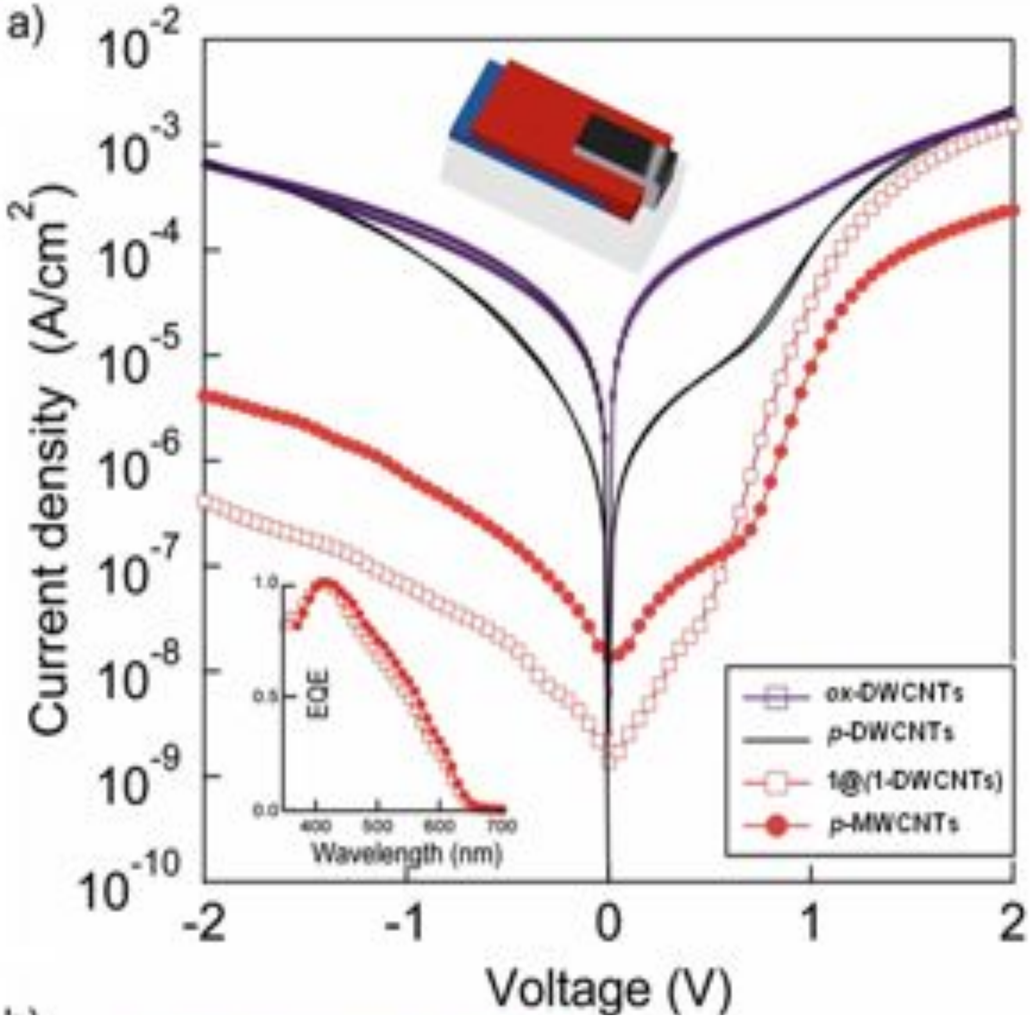




Adv. Funct. Mater. **2012**, *22*, 3315

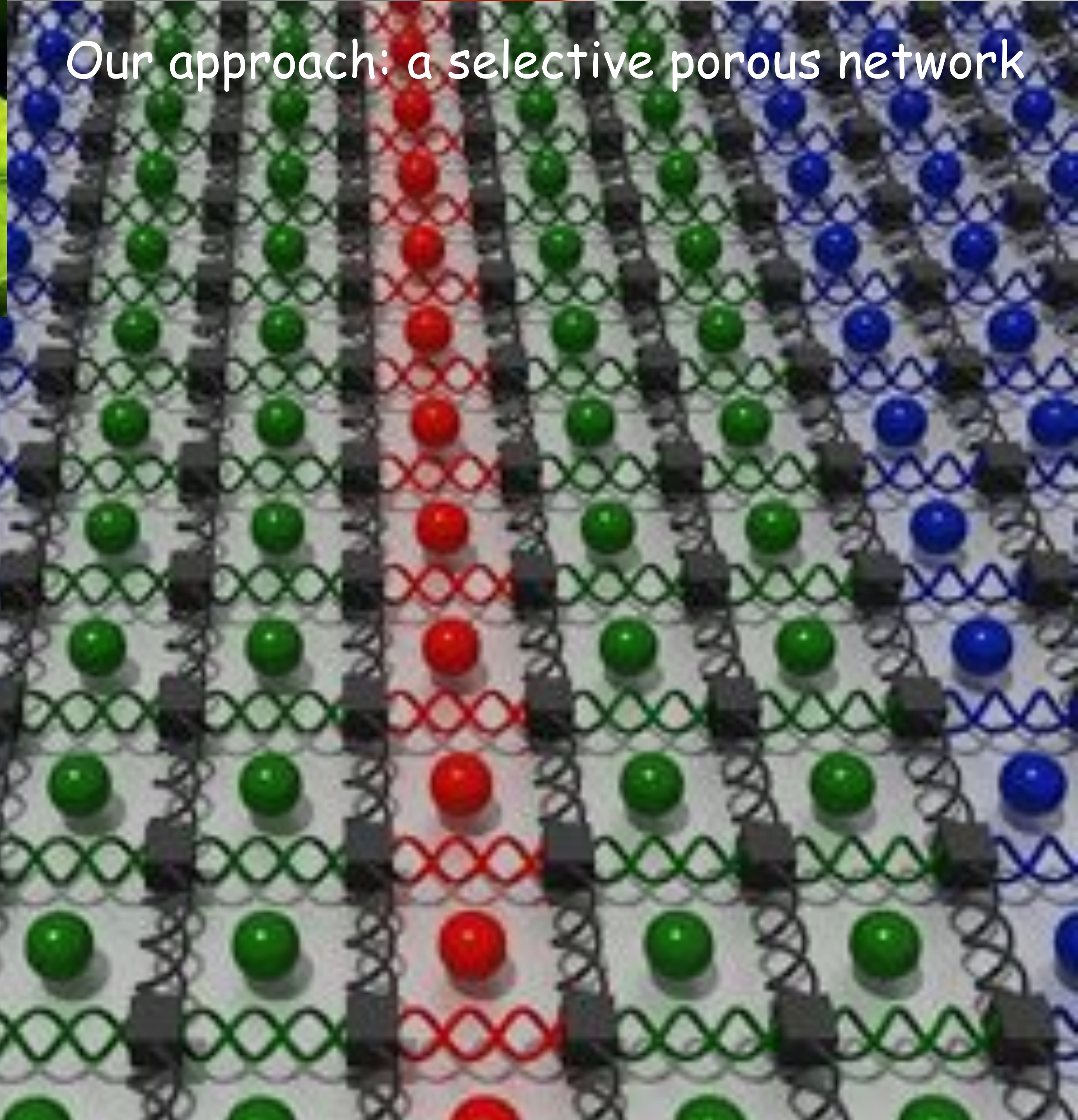

Fluorescence
¹O₂ Emission
I / a.u.
2.0
1.5
1.0
0.5
0.0
600
650
700
750
800
λ / nm
UV-Vis Adsorption
Ox-DWCNTs
1230
1260
1290
1320

Organic Diode: Conductivity Experiments



Adv. Funct. Mater. **2012**, *22*, 3315

Our approach: a selective porous network

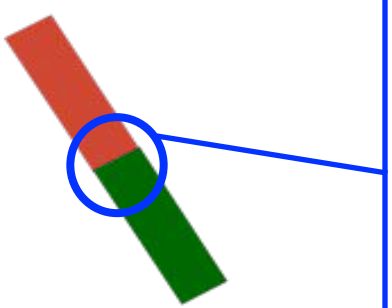


Molecular engineering

- **Multicomponent:** angular unit: control of the shape & linear unit: control of the size
- **Controlled**: fixed geometry of the molecules

Assembling Units	180º	60º	120º	90º
180º				
180º				

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



H-Bonding (4-120 kJ/mol)
R-X-H||||||Y-R_1

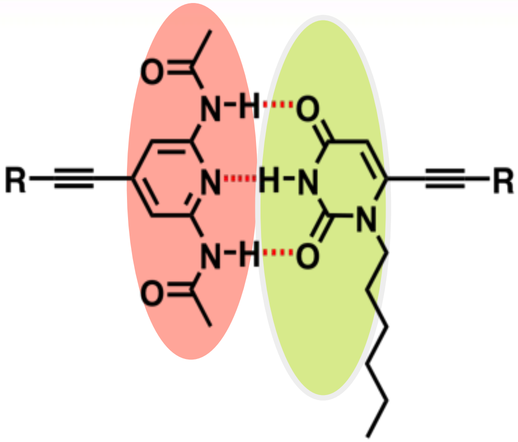
Metal Coordination (40-120 kJ/mol)
R-Y:||||||M||||||:Y-R_1

Dipolar Interactions (5-50 kJ/mol)
R → Y
Y ← R

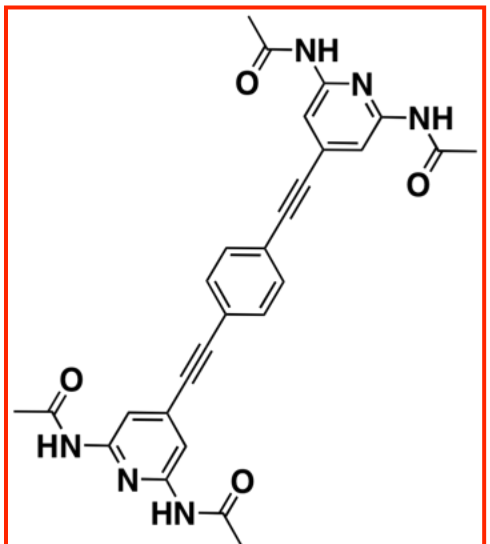
Halogen Bonding (20-40 kJ/mol)
R-N||||||X-R_1

Electrostatic (50-200 kJ/mol)
R-N||||||X-R_1

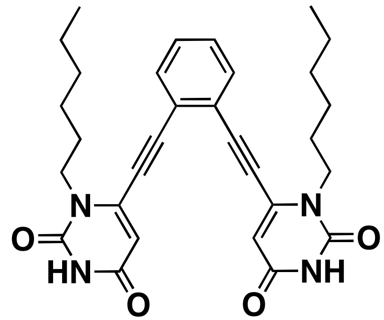
Triply H-bonded supramolecular polymers

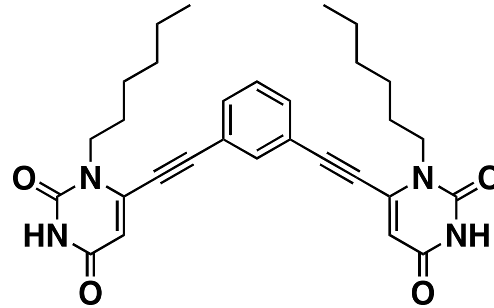


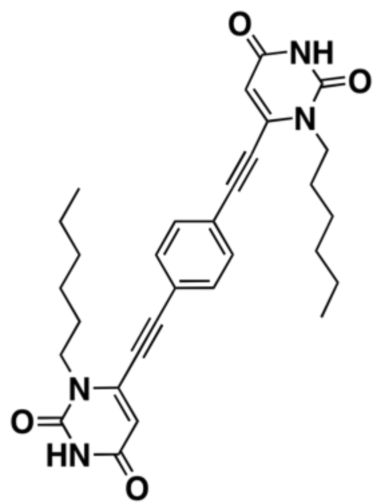
J. Chem. Soc. Chem. Commun., **1994**, *42*, 197

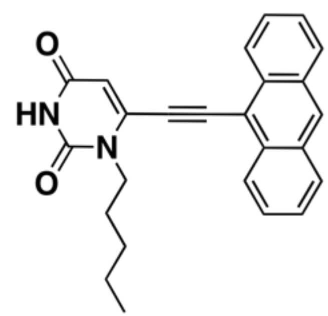


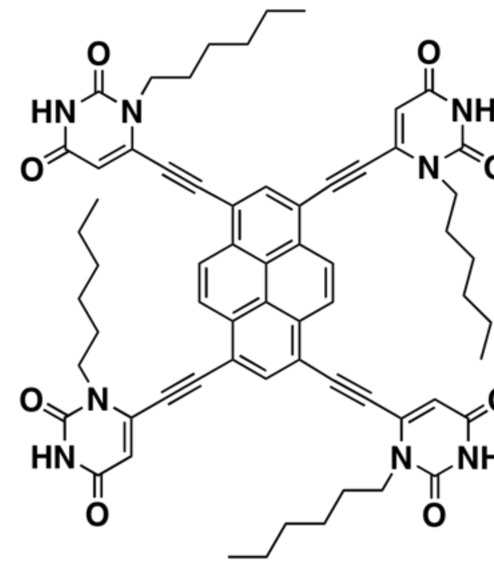
Dr. A. Llanes-Pallas





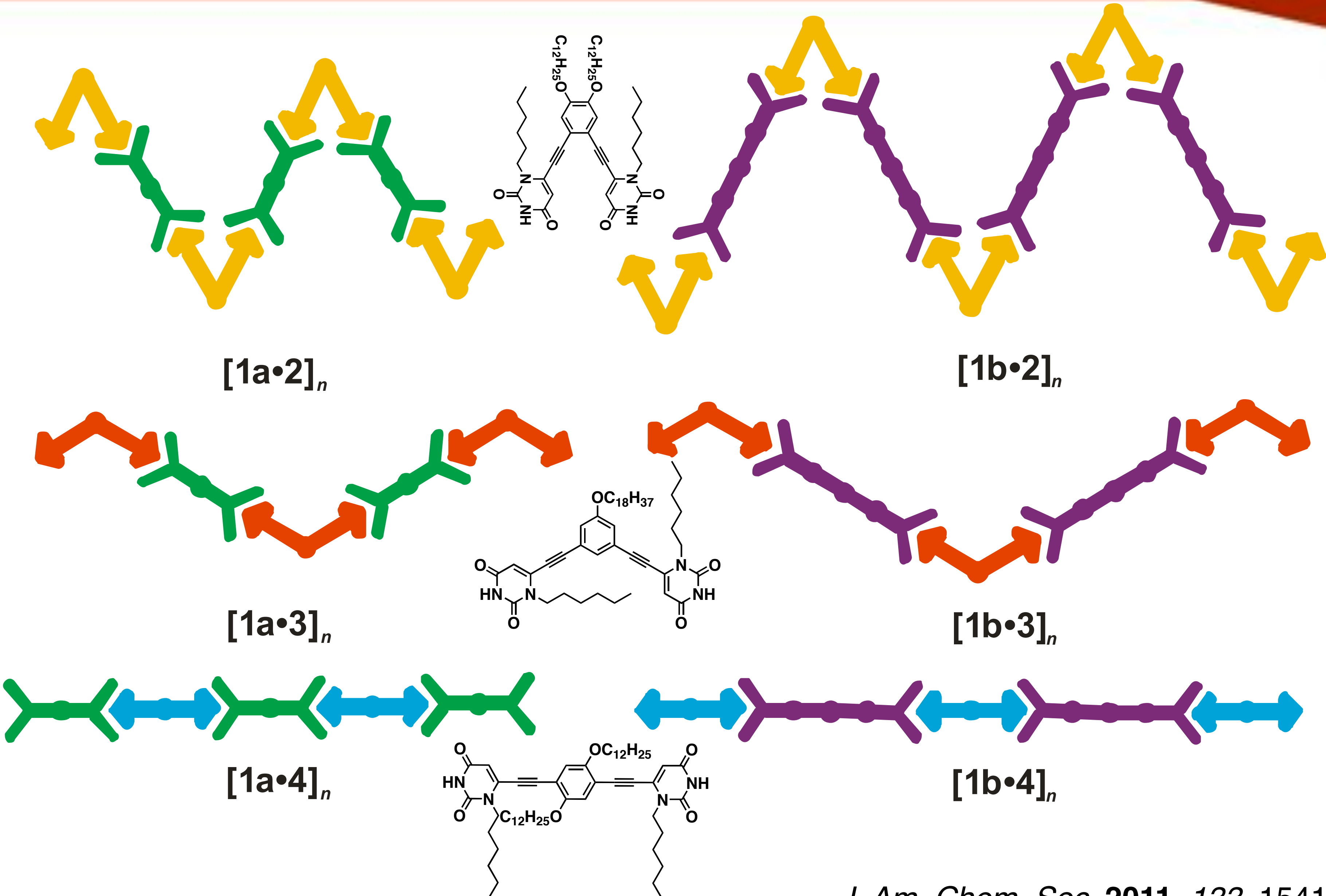






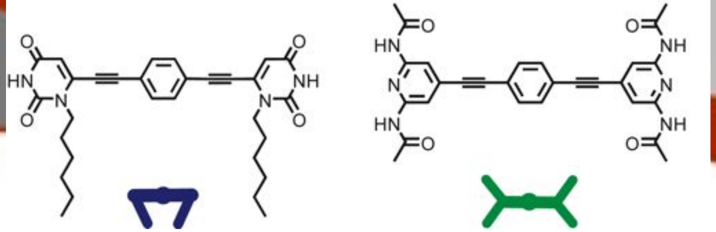
Angew. Chem. Int. Ed. **2008**, *41*, 7726; *J. Am. Chem. Soc.* **2009**, *131*, 509; *J. Am. Chem. Soc.* **2009**, *131*, 13062; *Chem. Commun.* **2009**, 3525; **HOT PAPER**; *Adv. Funct. Mater.* **2009**, *19*, 1207.

Triply H-bonded supramolecular polymers

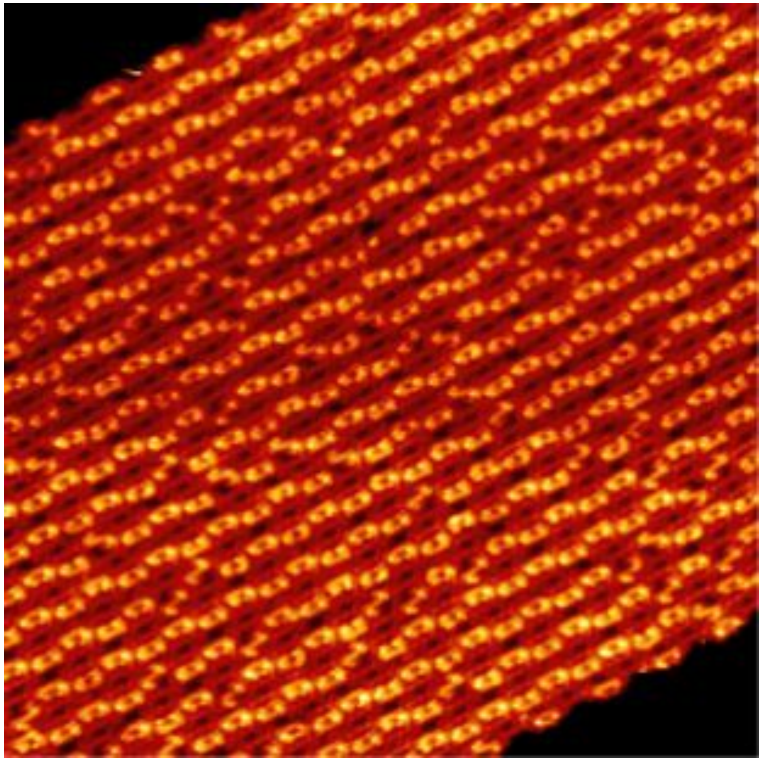


J. Am. Chem. Soc. **2011**, *133*, 15412

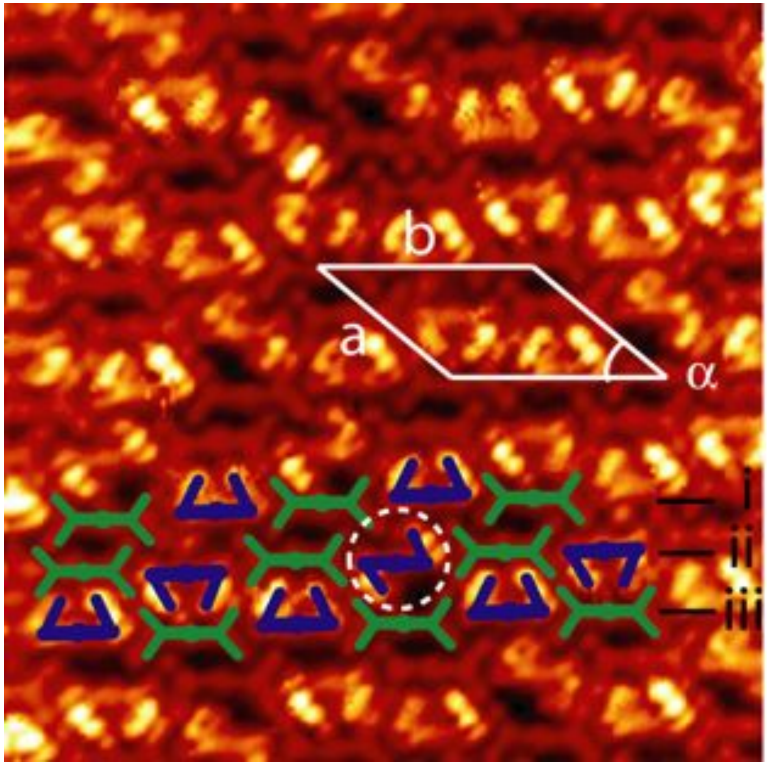
Linear Assemblies on Ag(111)



In coll. with M. Stohr (Univ. Groningen)



41.5×41.5 nm^2

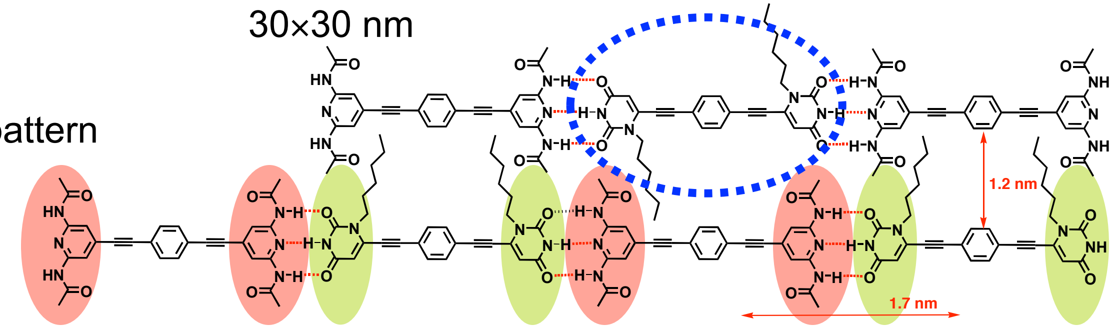


30×30 nm

Surface: **Ag(111)**
Tip: **Pt-Ir**
T: 383 K

Proposed
self-assembled pattern

3.7 × 2.4 nm
α ≈ 58 ± 4°



Angew. Chem. Int. Ed. **2008**, *41*, 7726

Conclusions ?

Thanks to All !!!!

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MARIE CURIE ACTIONS

SEVENTH FRAMEWORK PROGRAMME

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