CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

IEM MONTPELLIER

Constitutional sol-gel transcription of nucleobases self-assembly codes

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Adaptative Supramolecular Nanosystems Group

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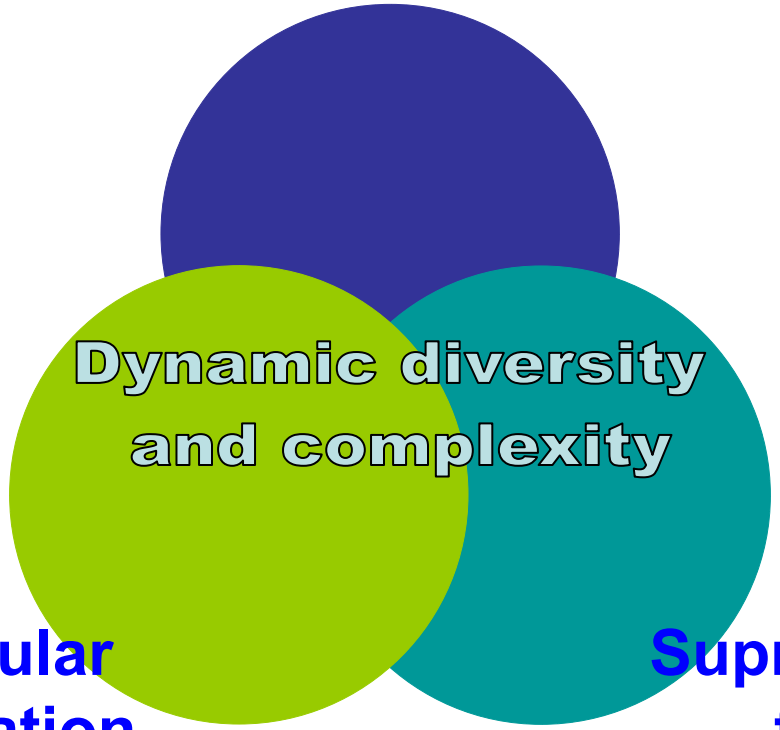
Informed molecular components



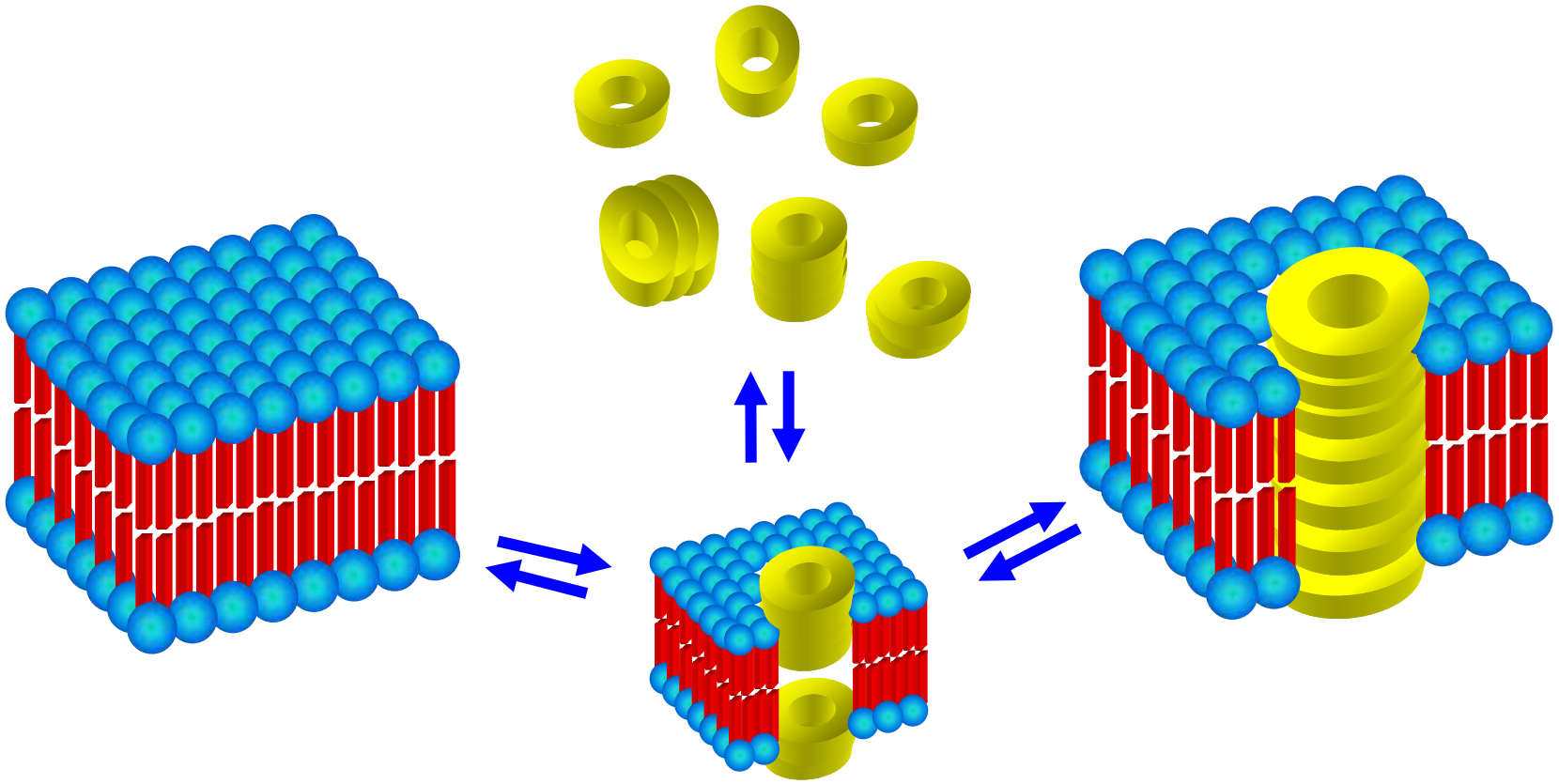
Supramolecular self-organization

Supramolecular function

The complexity of the supramolecular assemblies reveals the ways towards the fabrication of new functional materials

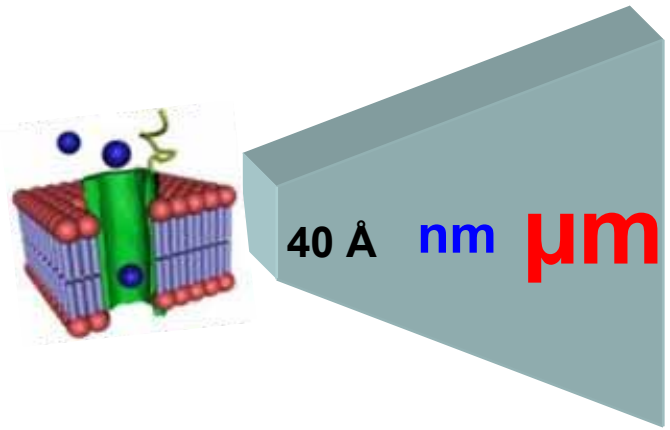
Going to functional supramolecular devices....by self-assembly

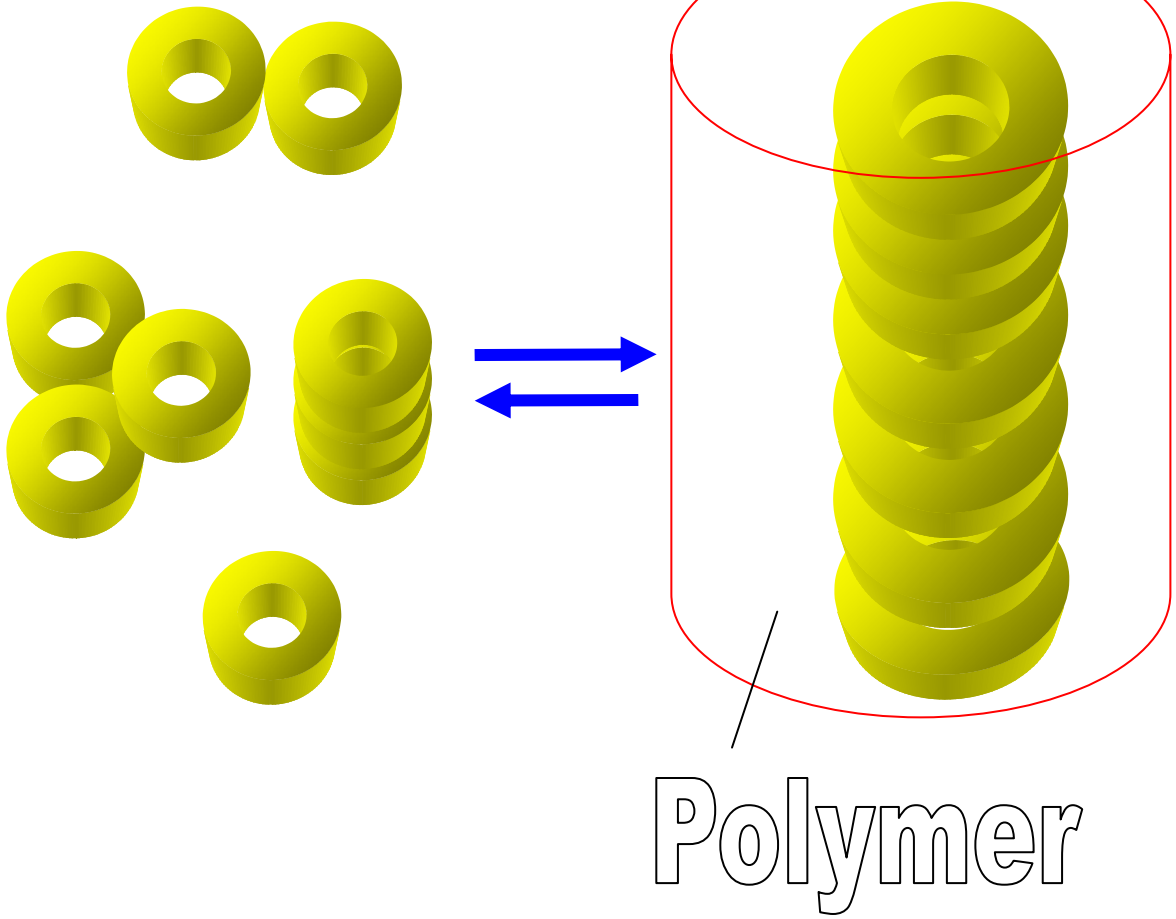
Despite the thermodynamic stability of the assemblies resulted from simple molecular components they are in dynamic equilibrium between monomer and supramolecular oligomers and only few examples clearly showed single-channel activity in lipid bilayers (40 Å)



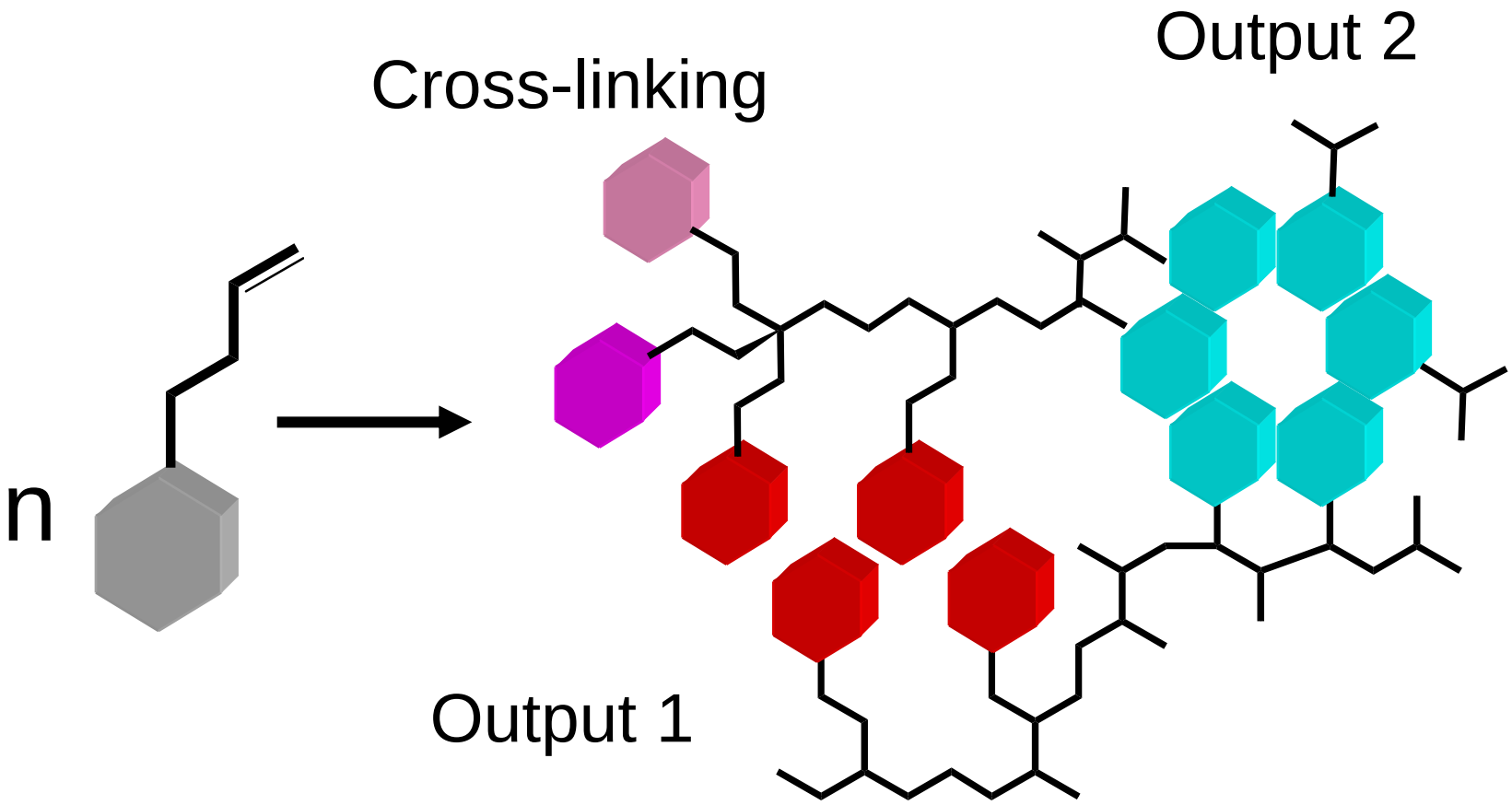
Going to functional supramolecular devices....by self-assembly

"Supracombimat"
exploring the chemical diversity by:
selection,
amplification,
fixation
in polymers





Conflicts between diferent levels of replication !



Self-organisation in supramolecular matter

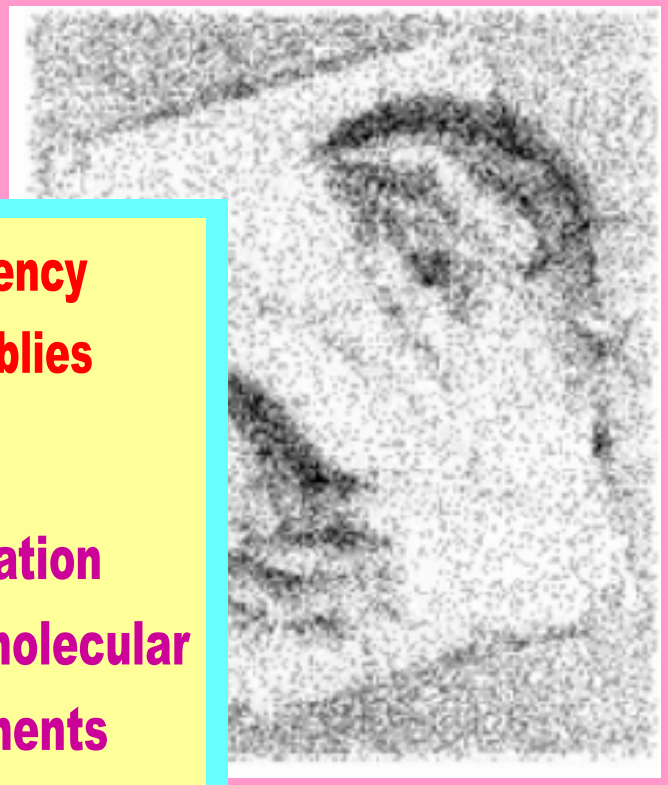
Self-disorganisation in macroscopic matter

Conflicts between levels of replication and aging!

Why do problems accumulate in self-organizing self-replicating & self-maintaining matter ?

Self-organisation in supramolecular matter

Self-disorganisation in nanometric matter

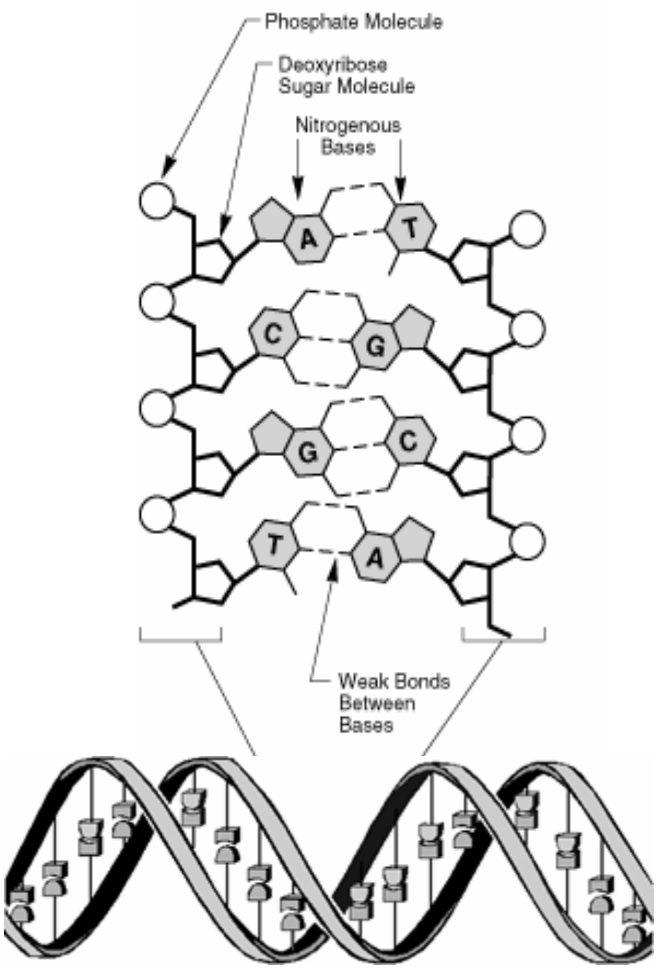


Improve the binding efficiency of supramolecular assemblies

Improve the communication efficiency between supramolecular and polymeric components

Adaptative reversible polymeric networks

Nucleobases as supramolecular synthons



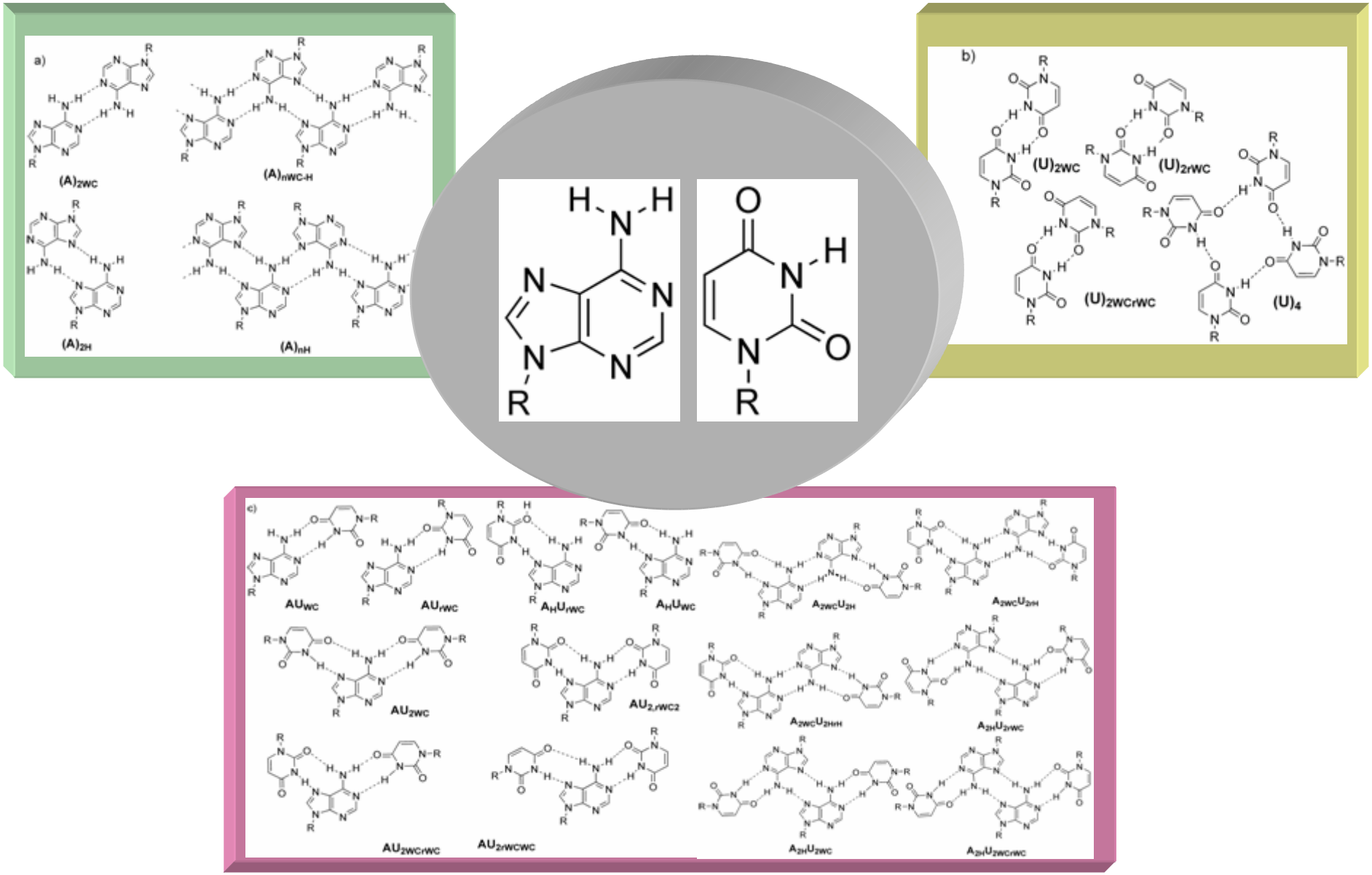
- High ability to form directionally controlled multiple intermolecular H-bonds of complementary nature - **Thermodynamic control**

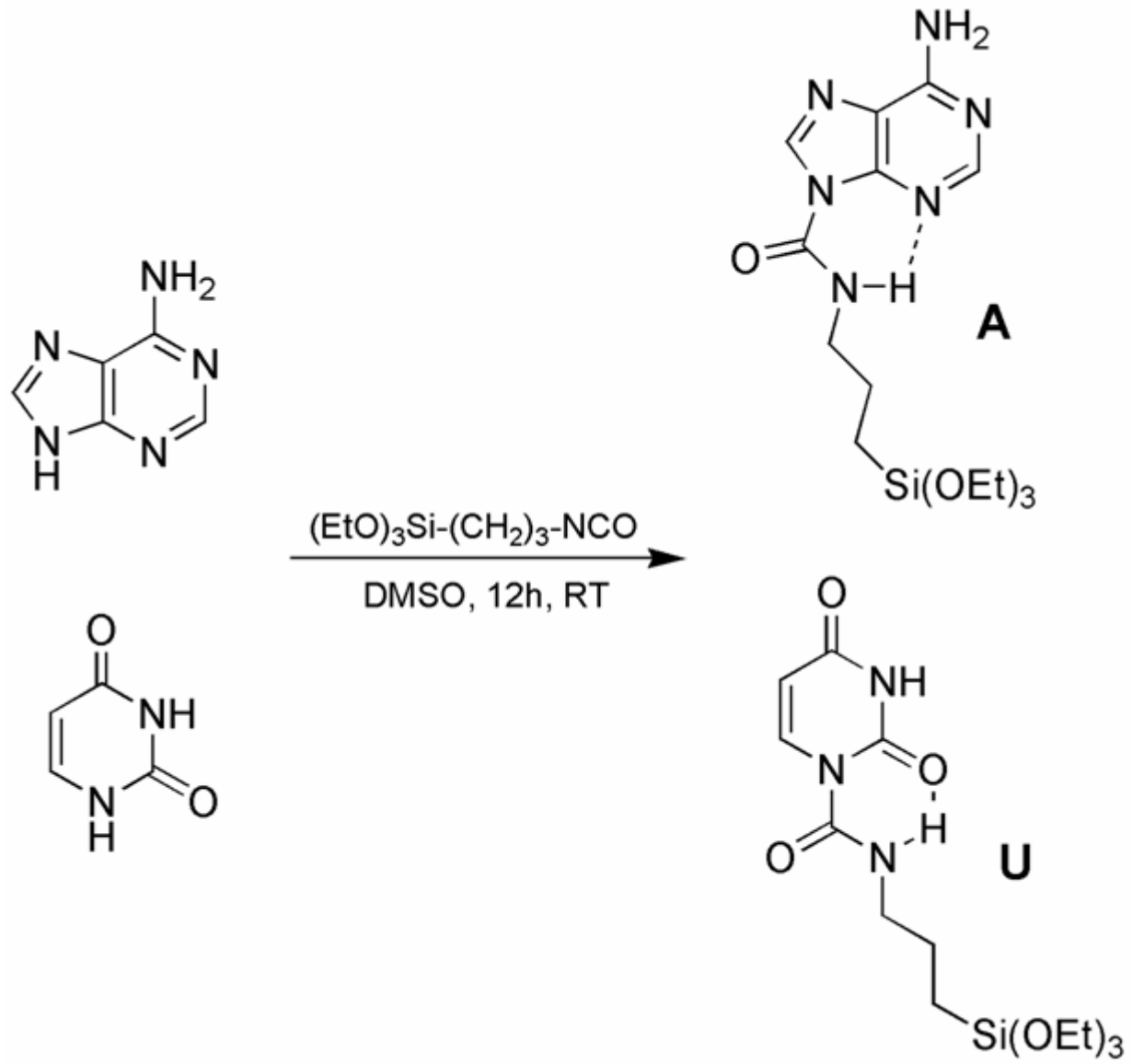
- They form a very diverse set of interconverting supramolecular entities *via* the combination of H-bond pairings- **Diversity**

- **High functionality**

J. L. Sessler et al. *Chem Commun.* **2005**, 1939 or *Chem Soc. Rev.*. **2007**, 314
J. T. Davis, *Angew. Chem. Int. Ed.* **2004**, *43*, 668
S. Shinkai *Angew. Chem. Int. Ed.* **2004**, *43*, 3279.
S. T. Rowan, *Chem. Soc. Rev.* **2005**, *34*, 9

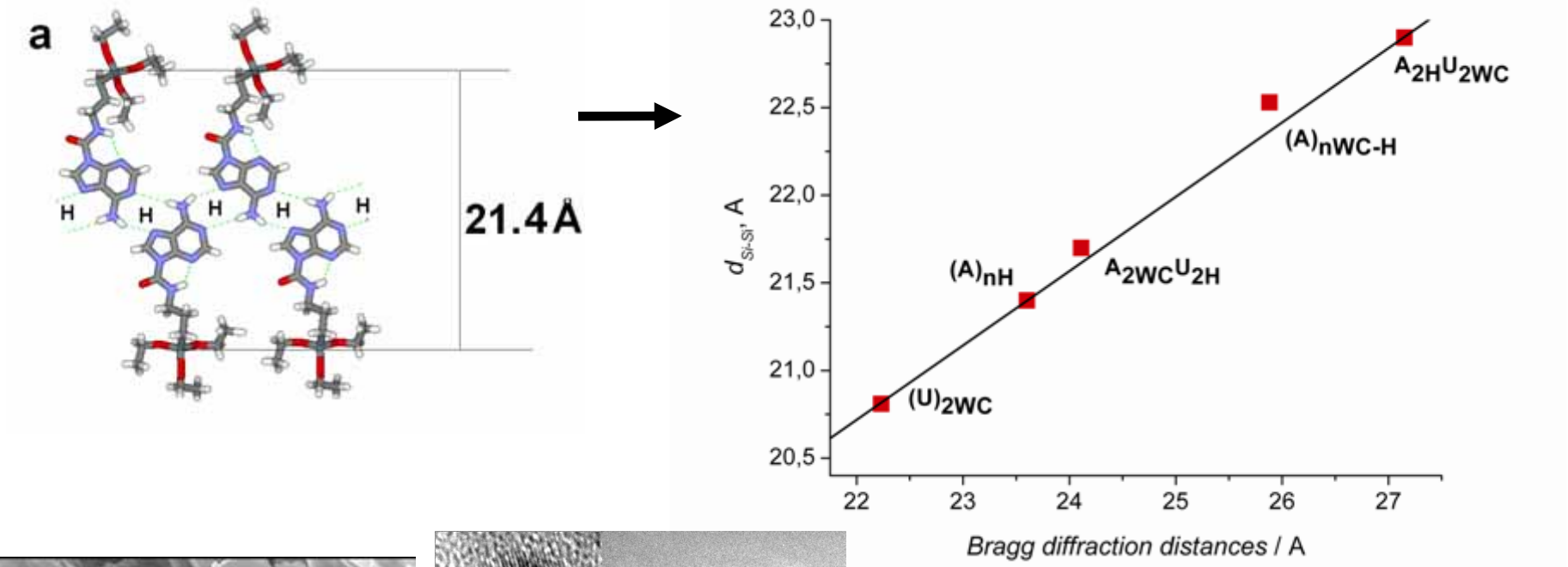
Diverse set of supramolecular entities may be generated by using only adenine and uracil

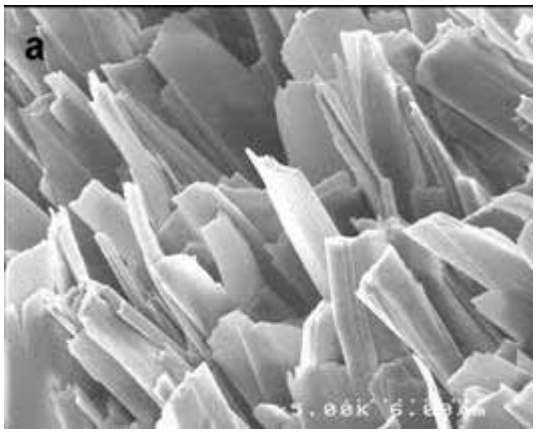


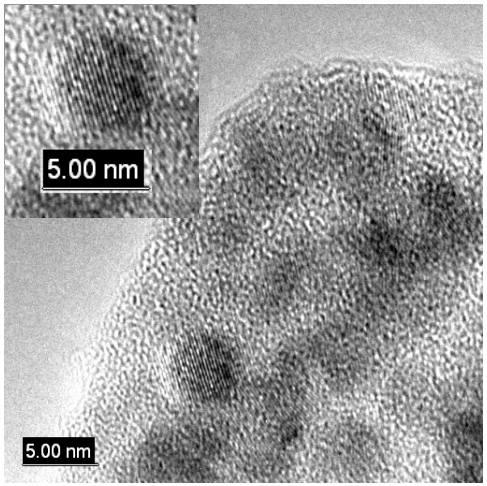


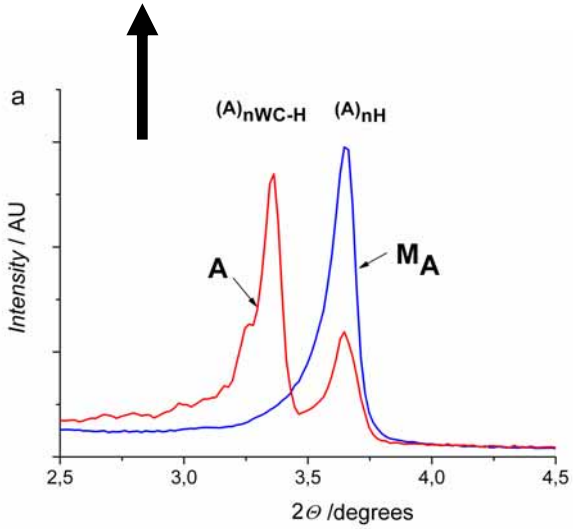
Chem. Eur. J. **2007** , *13,* 6792-6800

Correlation between calculated interplanar d_{Si-Si} distances and experimental interplanar Bragg diffraction distances.



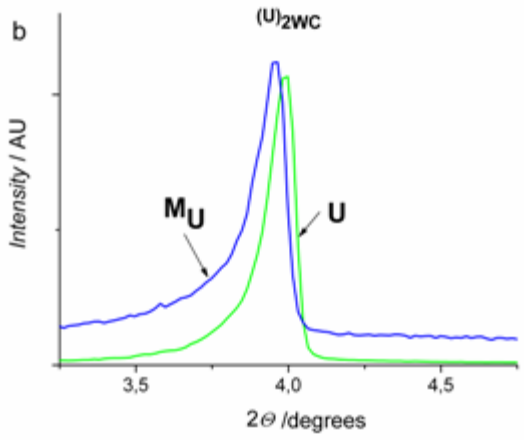


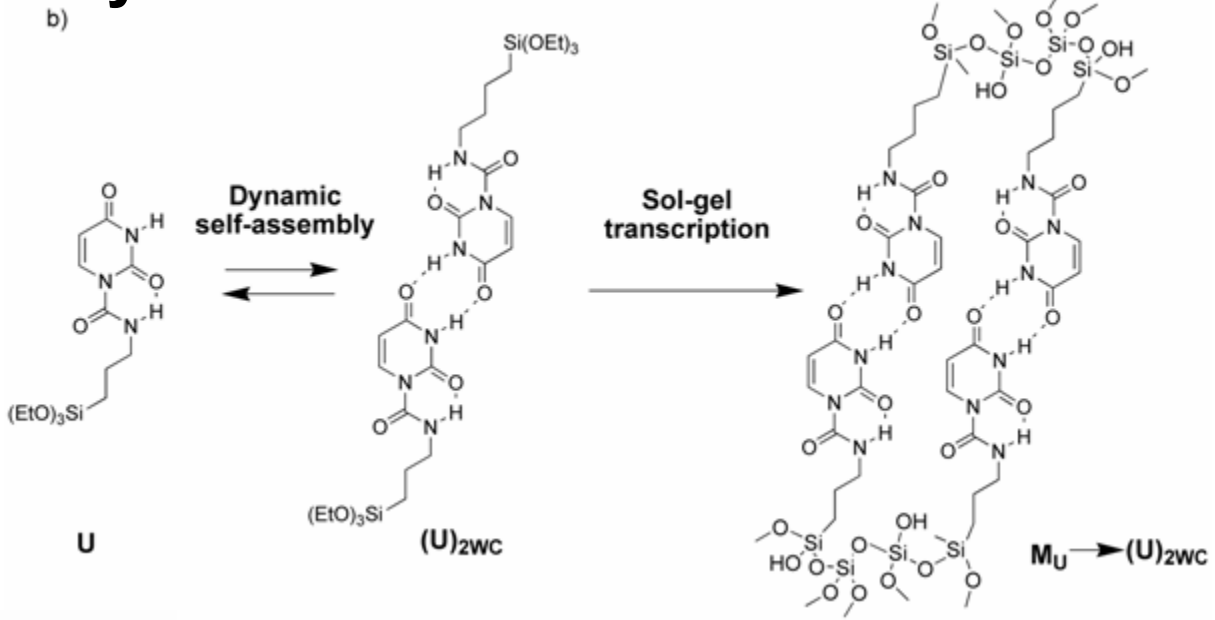


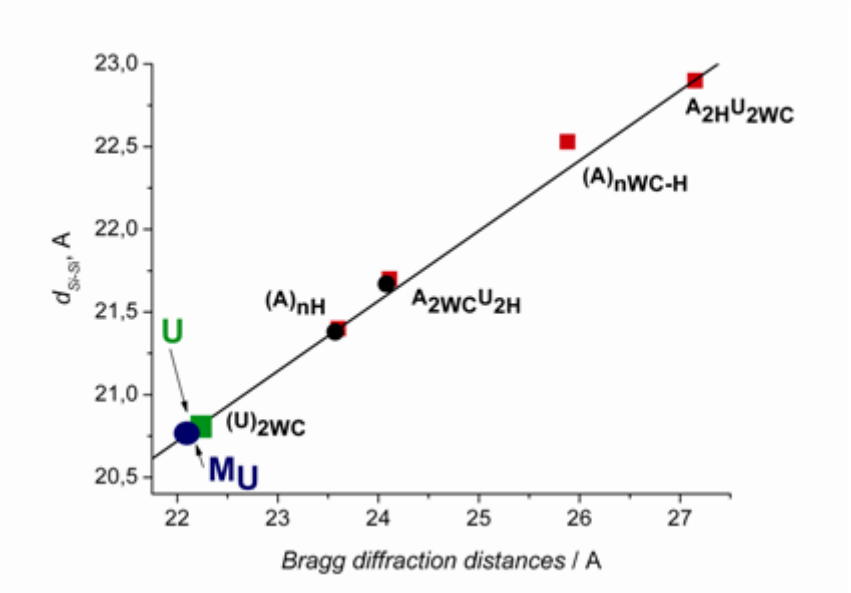


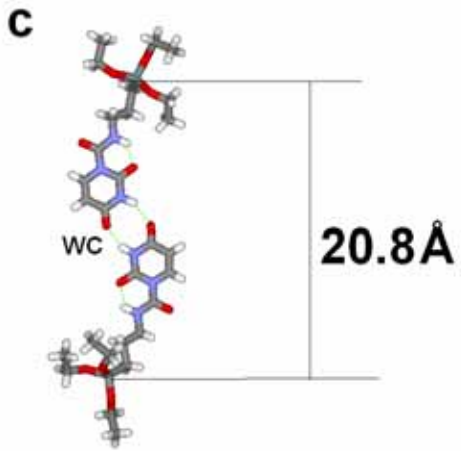
Chem. Eur. J. **2007** , *13,* 6792-6800

Constitutional Watson-Crick packing of the Uracil hybrid material



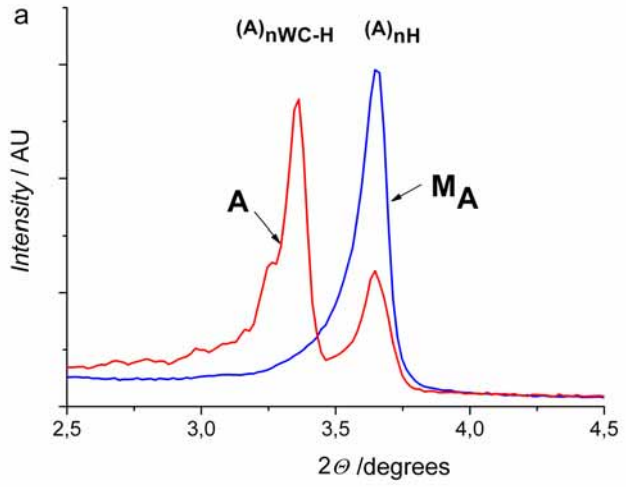


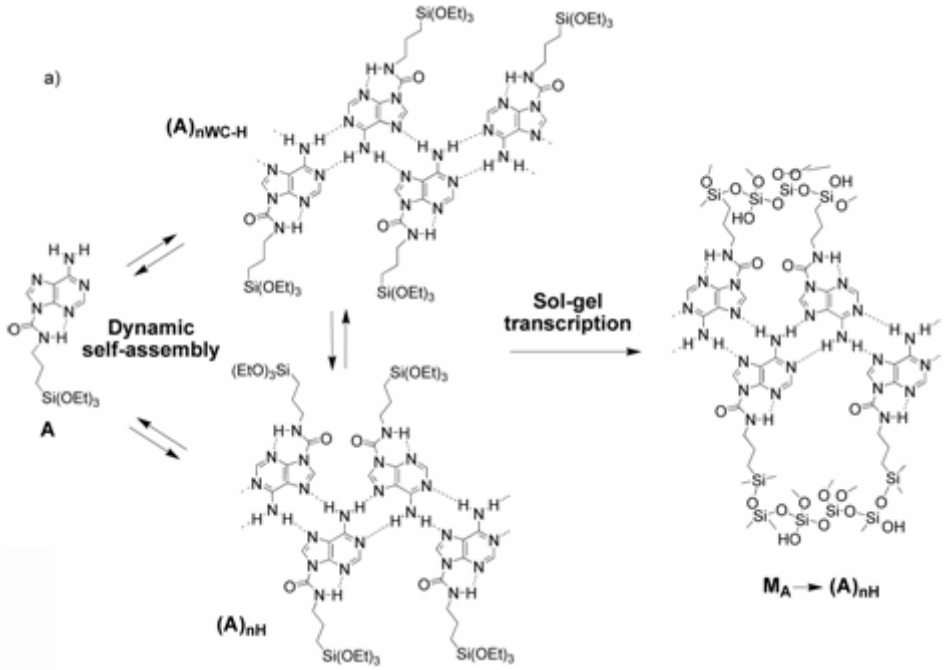


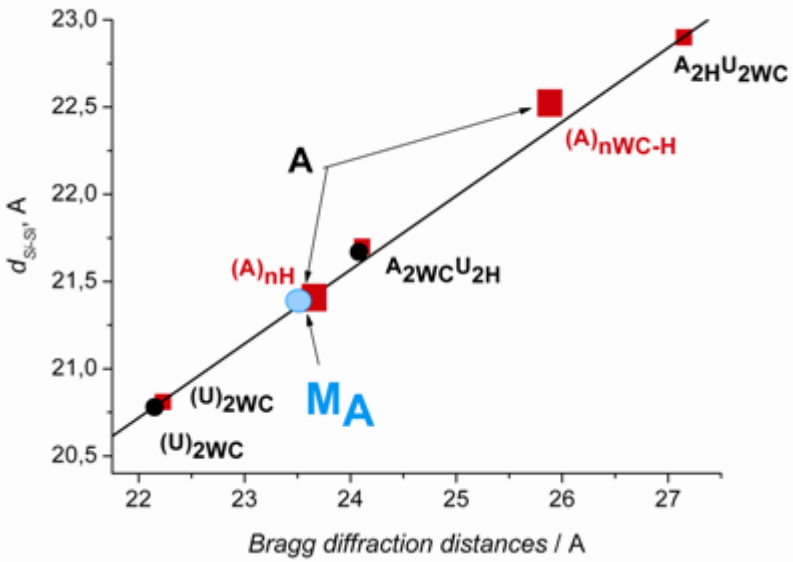


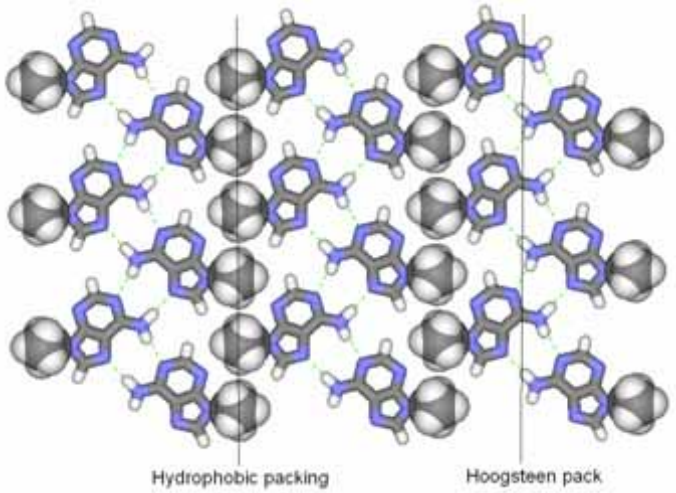
Chem. Eur. J. **2007** , *13,* 6792-6800

Constitutional Hoogsteen packing of the Adenine hybrid material



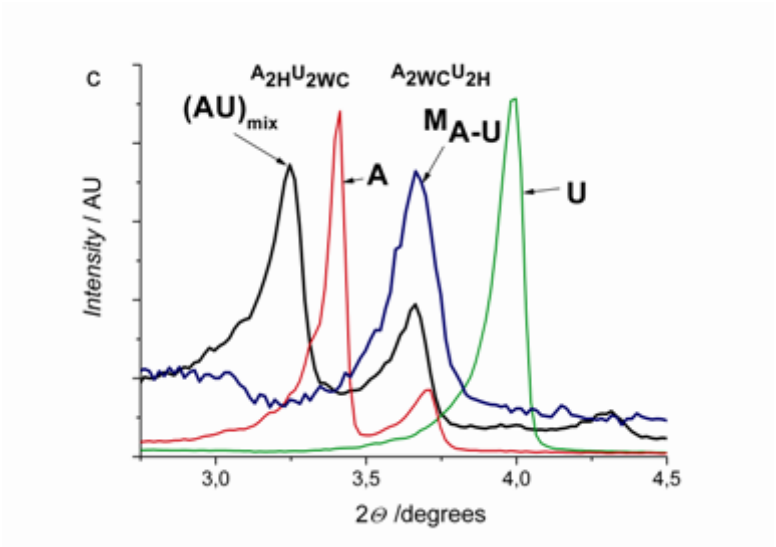


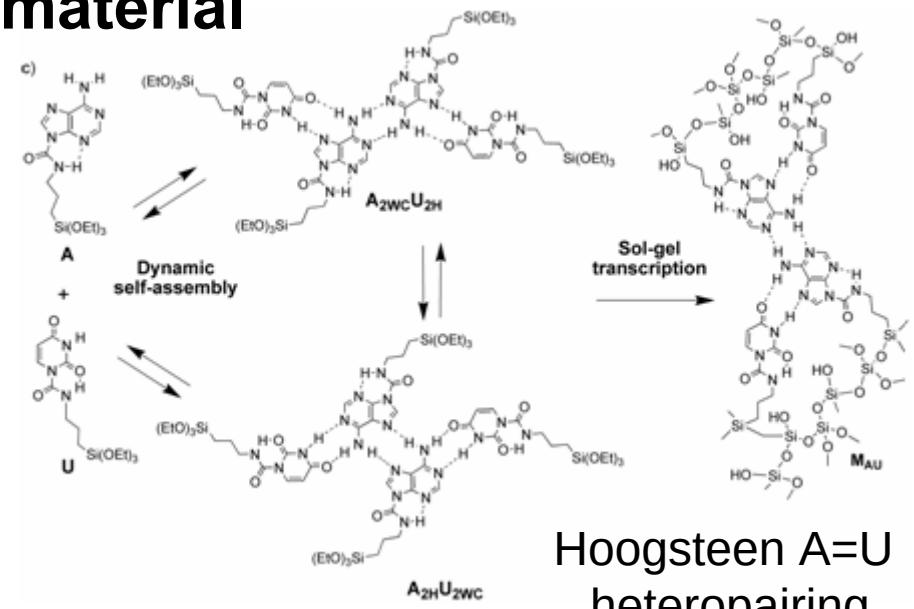




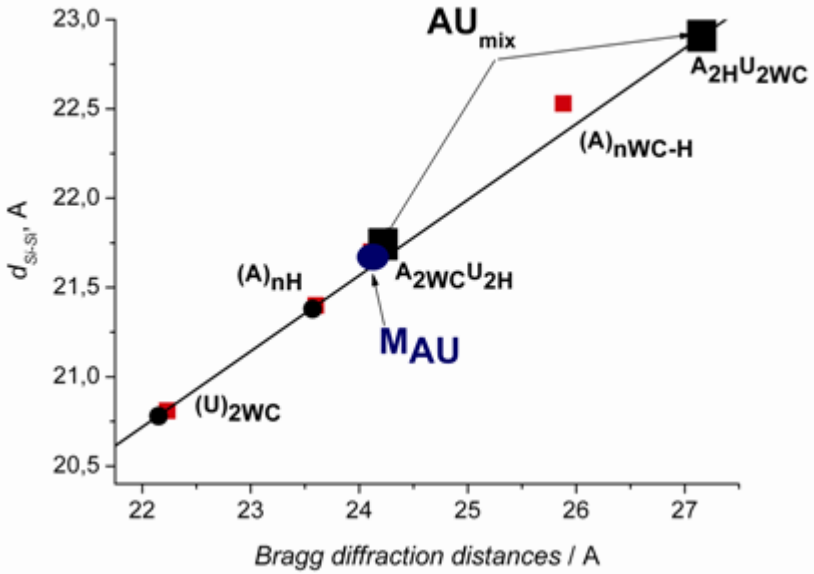
Chem. Eur. J. **2007** , *13,* 6792-6800

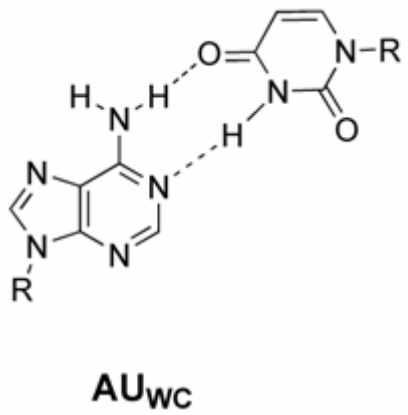
Constitutional $A_{2WC}U_{2H}$ packing of the Adenine-Uracil hybrid material

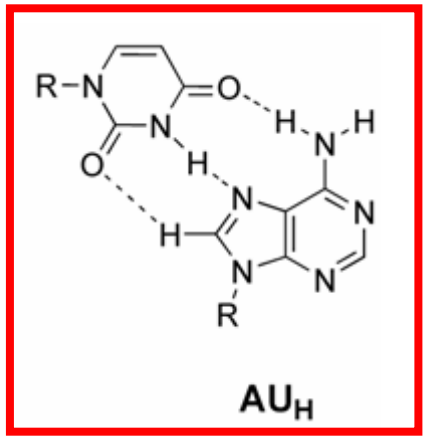




Hoogsteen A=U heteropairing

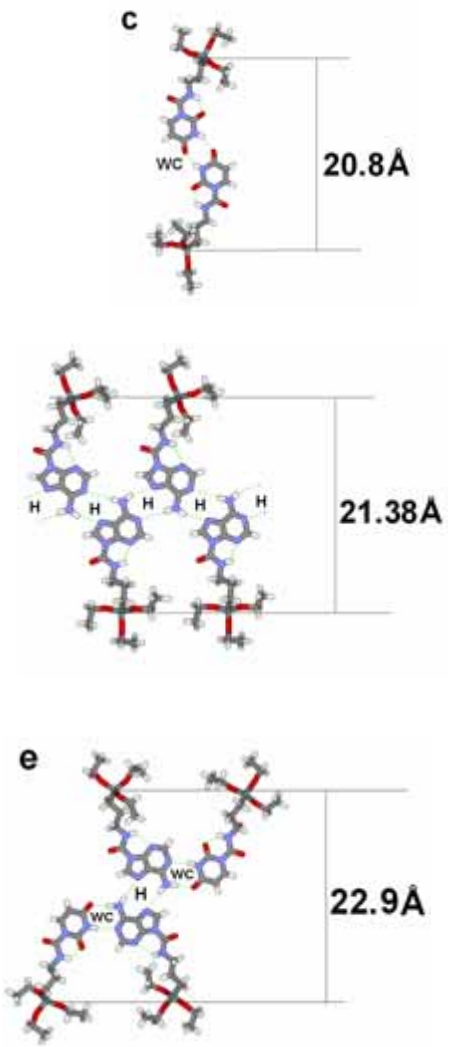


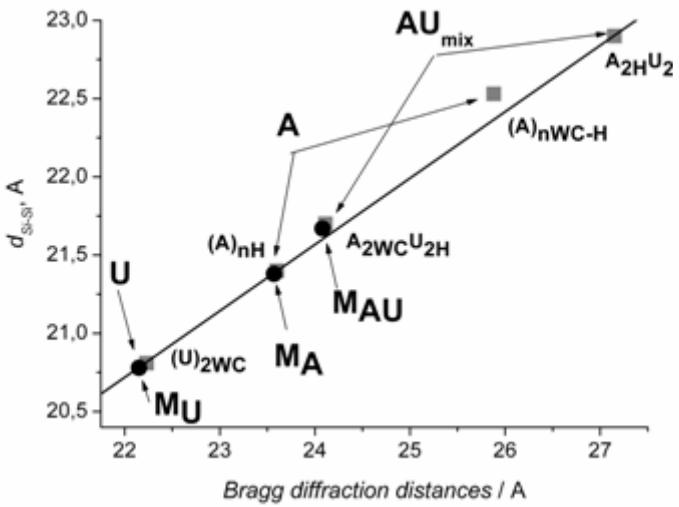


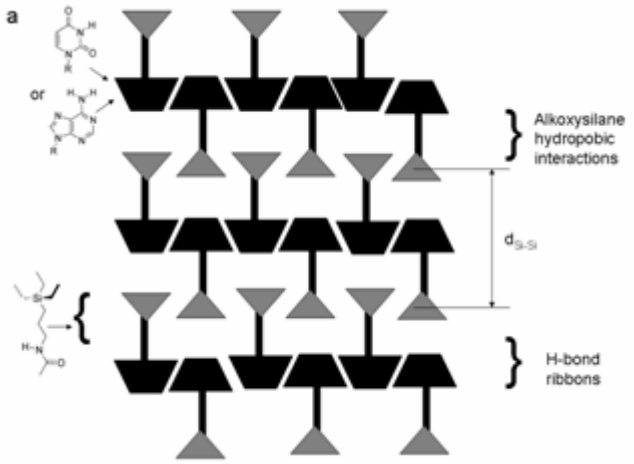


M. C. Etter et al., *J. Am. Chem. Soc.* **1993**, *115*, 4411
F. Diederich et al. , *Chem. Eur. J.,* **2002**, *8*, 118.
Ziemmerman et al.*J. Am. Chem. Soc.* **2007**, *129*, 934

Toward a constitutional transcription of base-pairing codes in hybrid materials.

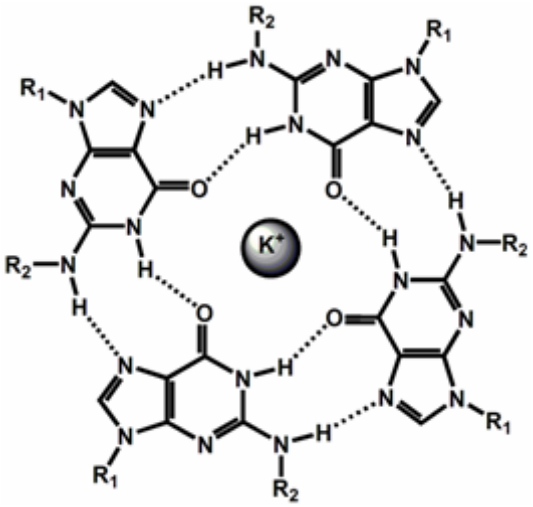




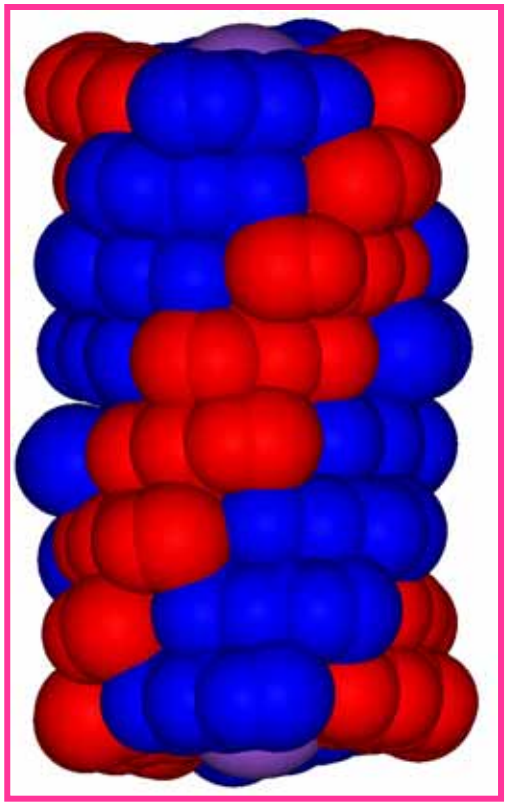


Wiley Encyclopedia of Chemical Biology, **2007** doi:10.1002/9780470048672.wecb527

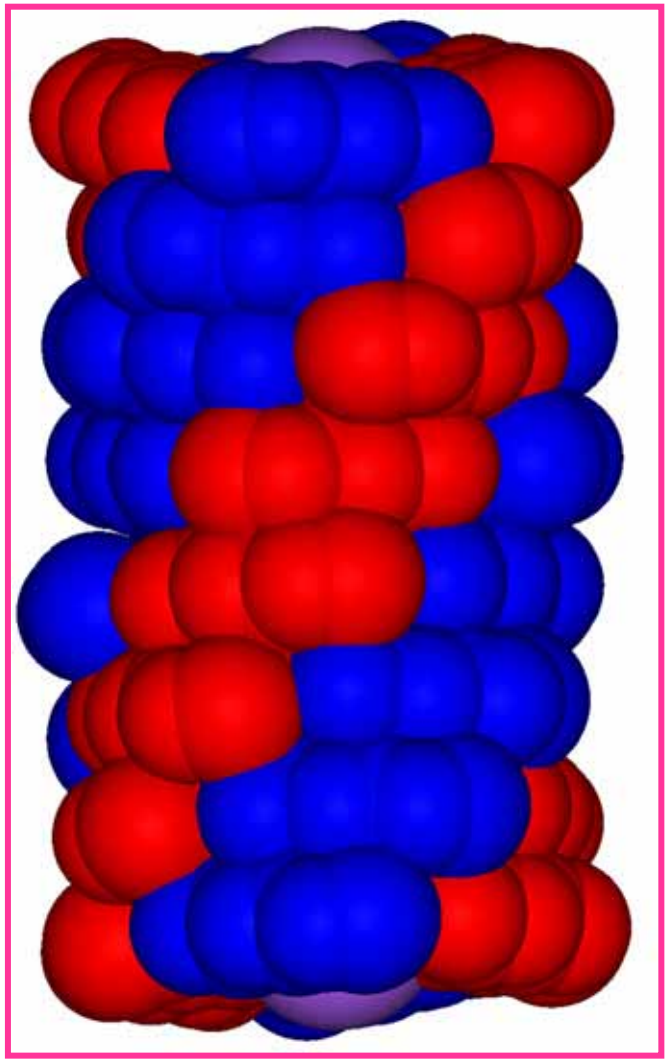
G4-quadruplex

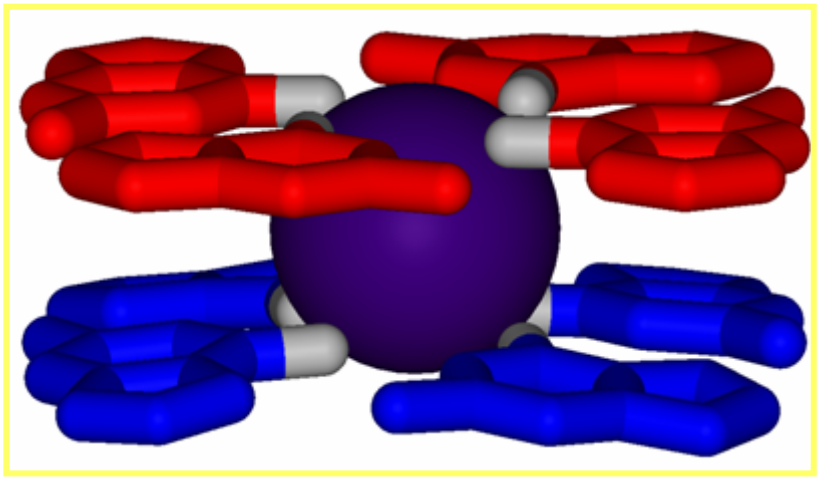


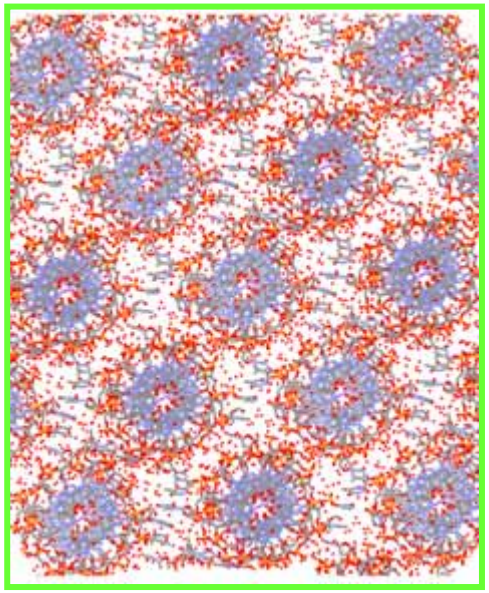
- identification in 1962
- Tubular H-bond superstructures stabilized in the presence of ions (K^+, Na^+, Ba^{2+},...)
- Presumed ion-channelling functions: although stable in organic solvents they do not seem to have defined transport functions in hydrophobic membranes
- Barrel-stave (Matile)
  Lipophilic, calix[4]arene (Davis, Gottareli, Spada)
  8-aromatic -guanosine- (Sessler) conjugates have been used to stabilize the formation of G-quartets.



G4-quadruplex

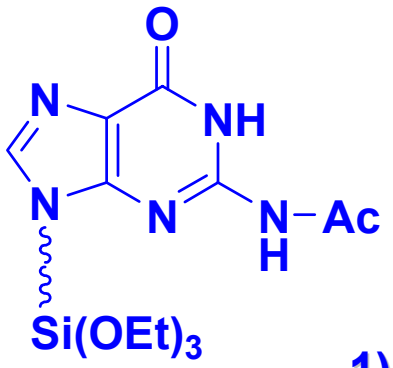






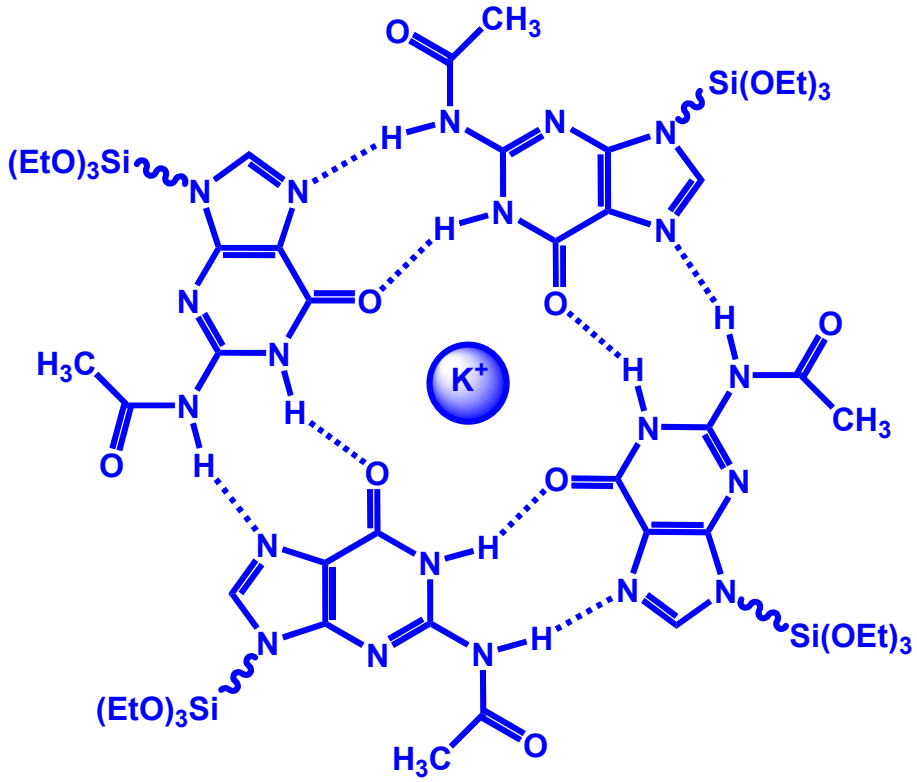
K. Phillips, Z. Dauter, A.I.H. Murchie, D.M.L. Lilley, B. Luisi, *J.M.B.,* 1997, 171

G4-quadruplex

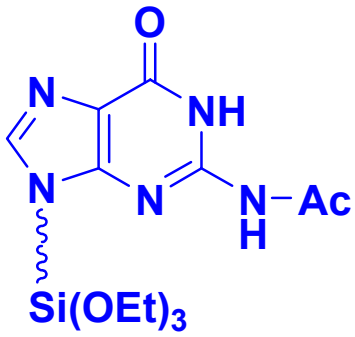


KTf, NaTf, $BaTf_2$

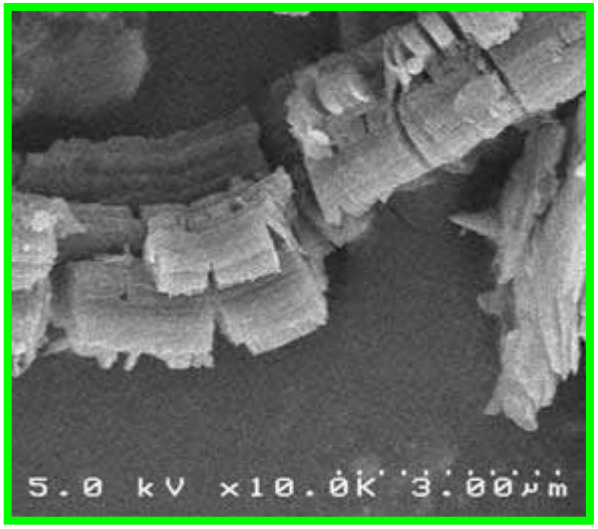
1) Self-assembly
2) Sol-gel



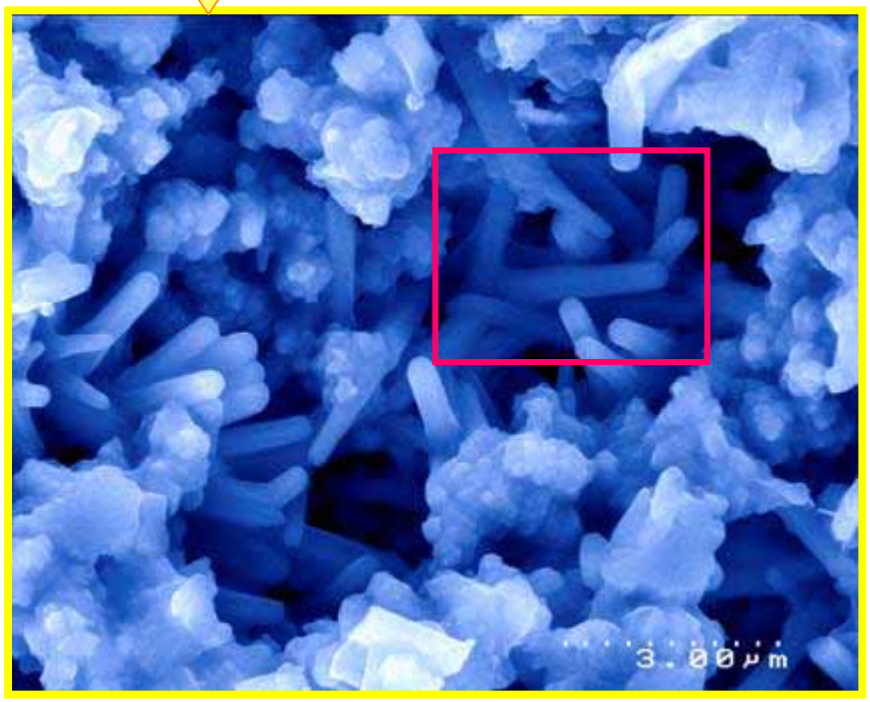
Angew. Chem. Int. Ed. **2007**, 46, 4268.

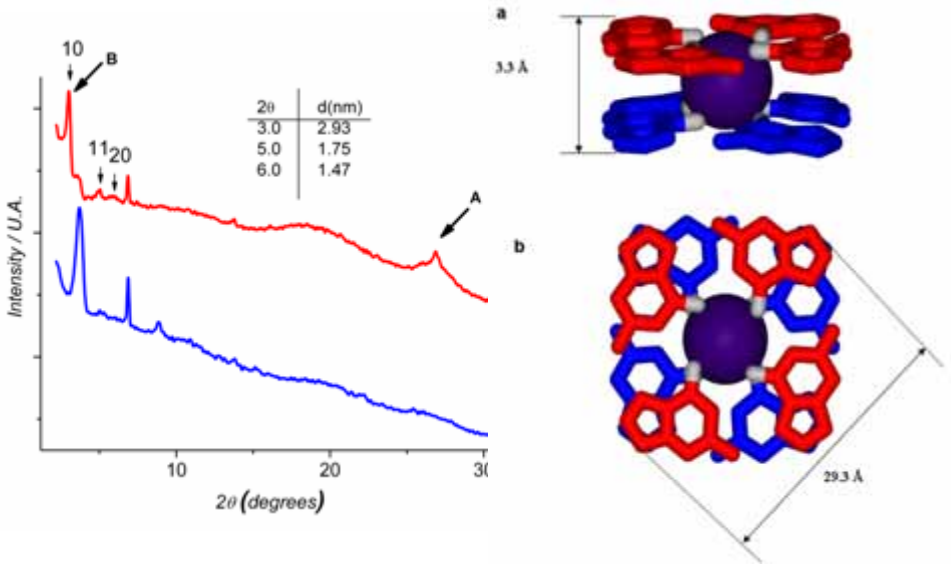


Sol-gel

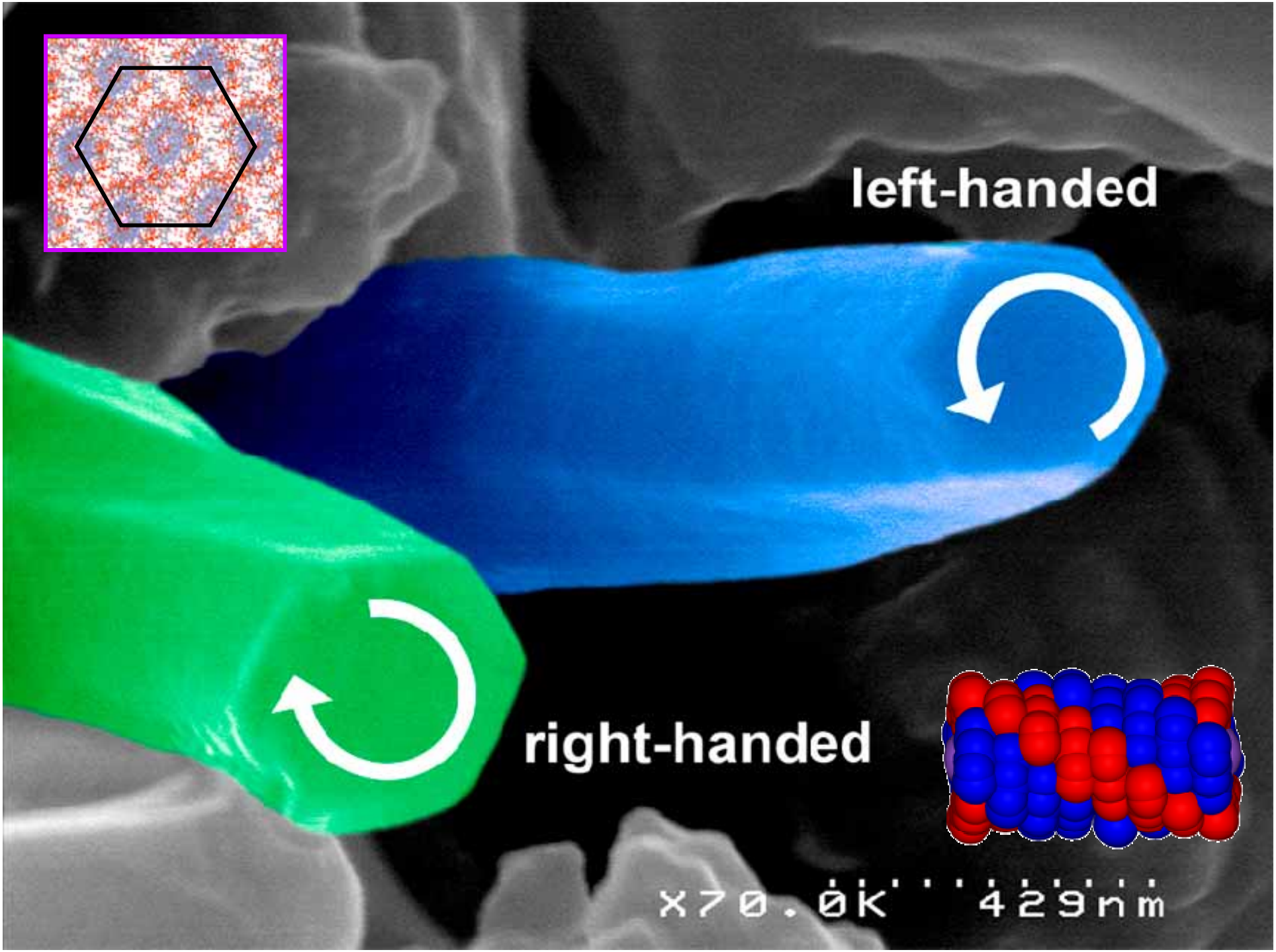


Sol-gel, KTf

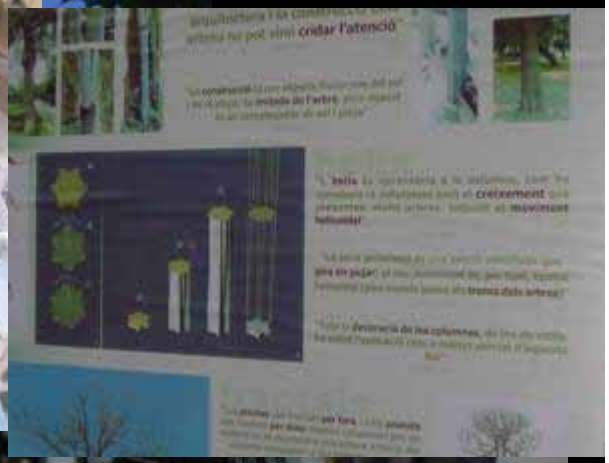


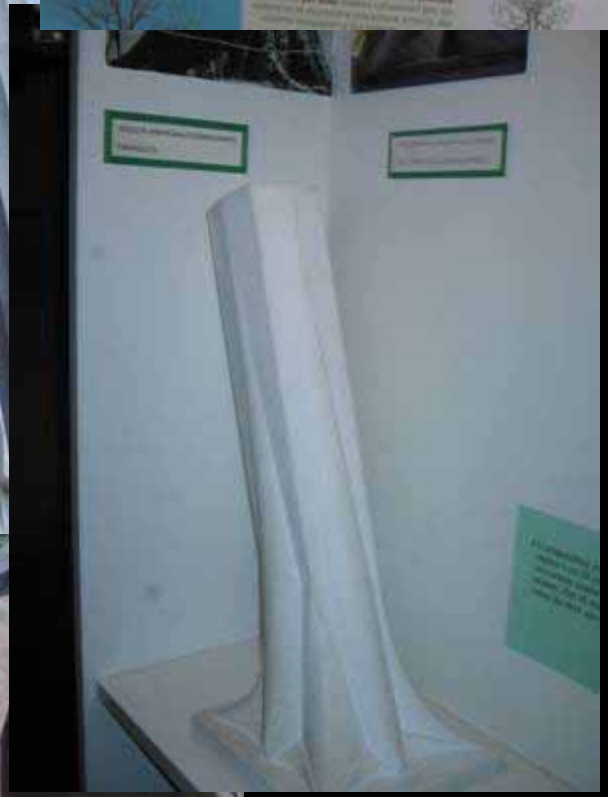


Angew. Chem. Int. Ed. **2007**, 46, 4268.

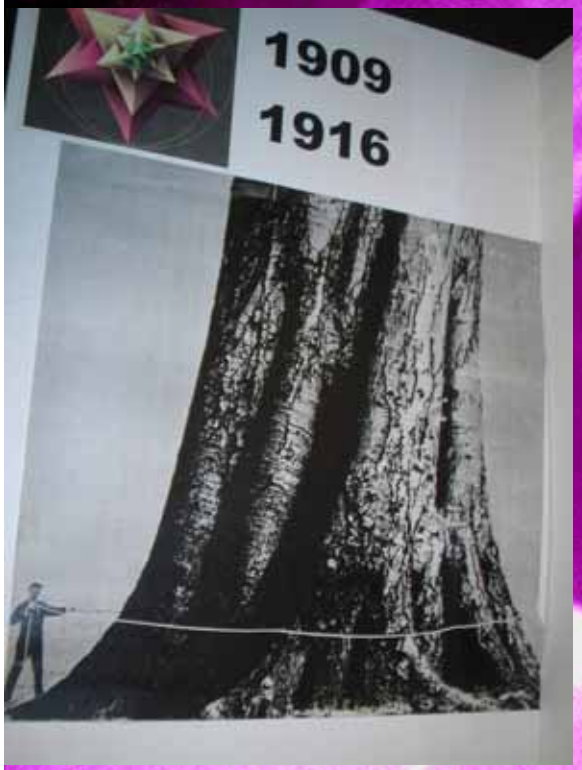

left-handed
right-handed
x70.0k 429nm

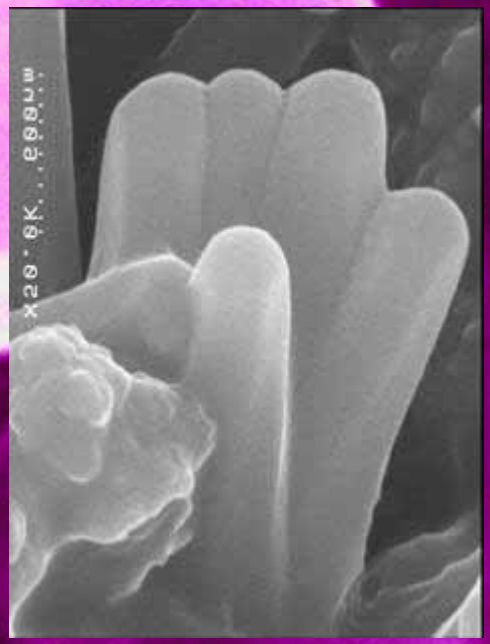
Antonio Gaudi
Sagrada Familia
Barcelona



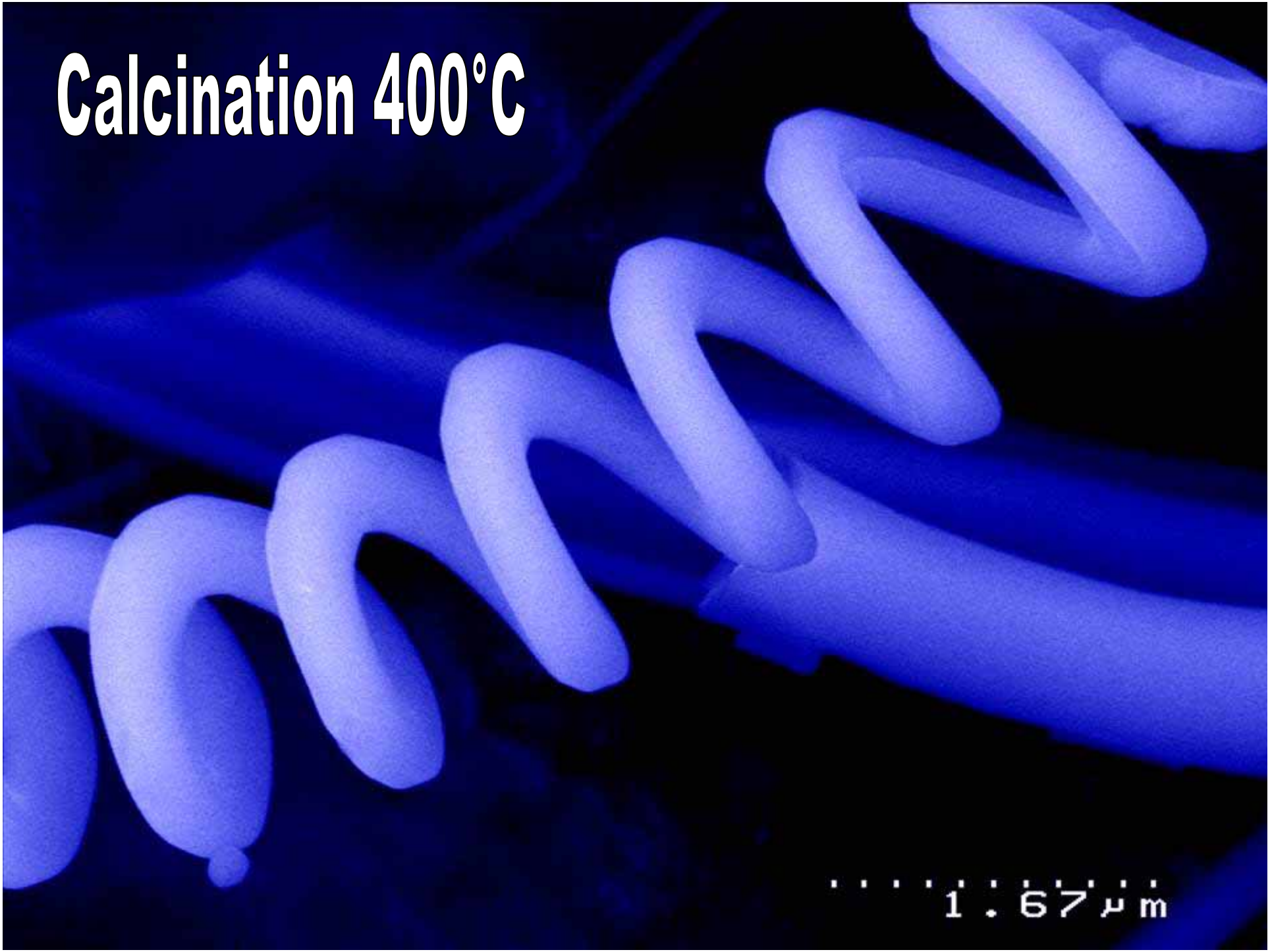


Chiral nanosequoias !

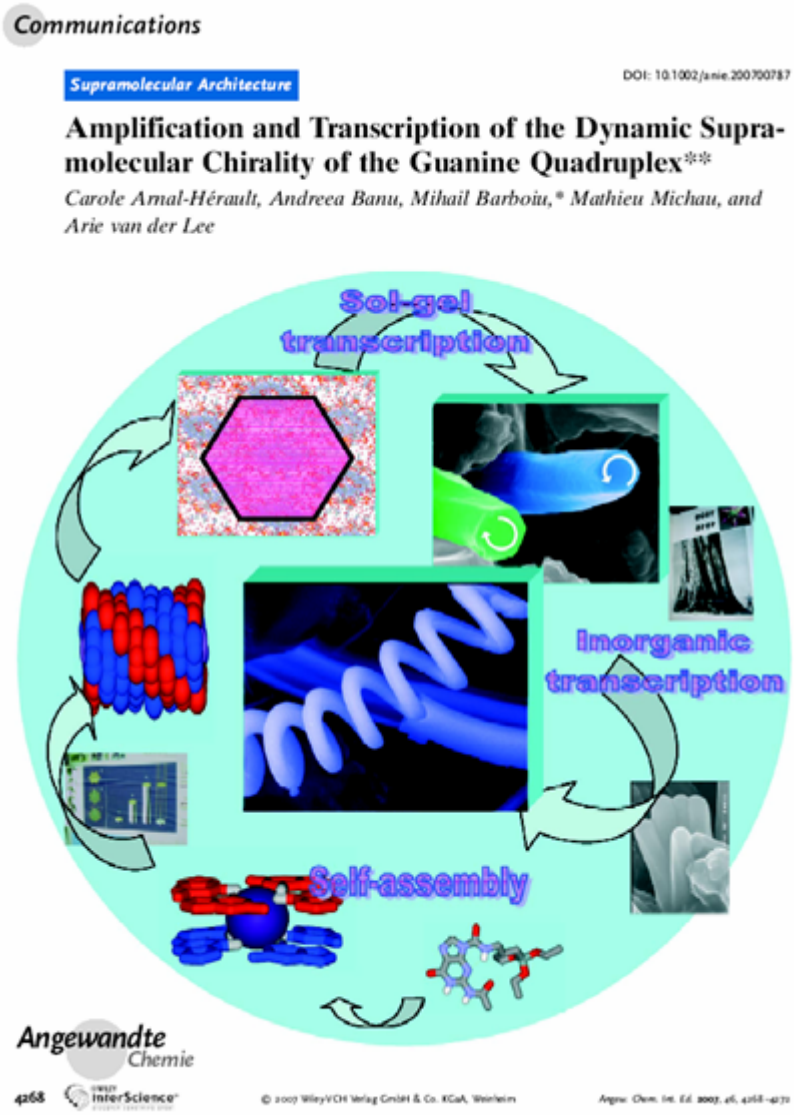




X70.0K 429nm


Calcination 400°C
1.67µm

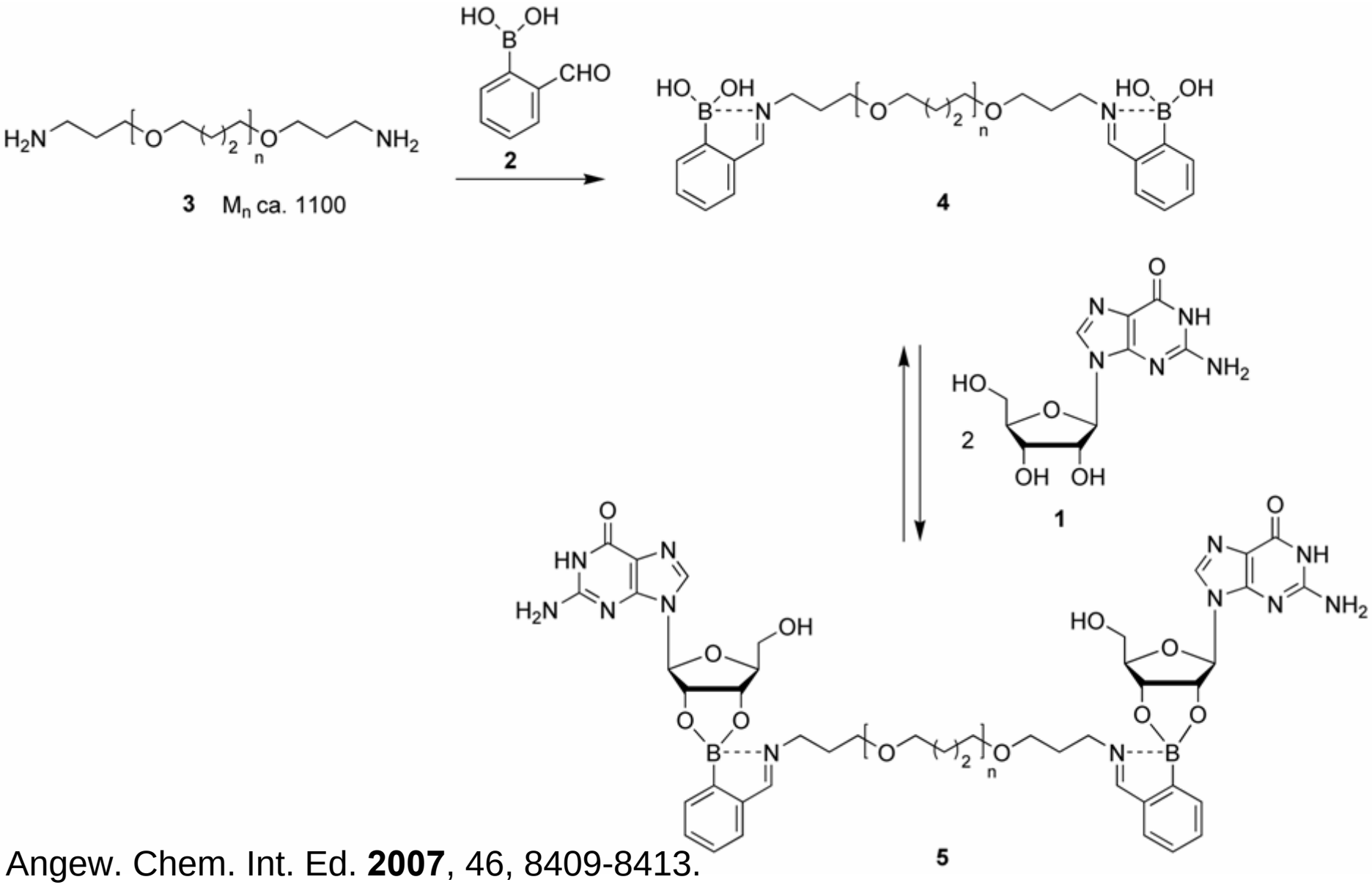
Transcription and amplification of supramolecular chirality



Complex dynamic feedback between *achiral* molecular partners gives rise to the *chiral* supramolecular architecture which can be amplified with a collective behaviour by using the a well adapted transcription strategy.

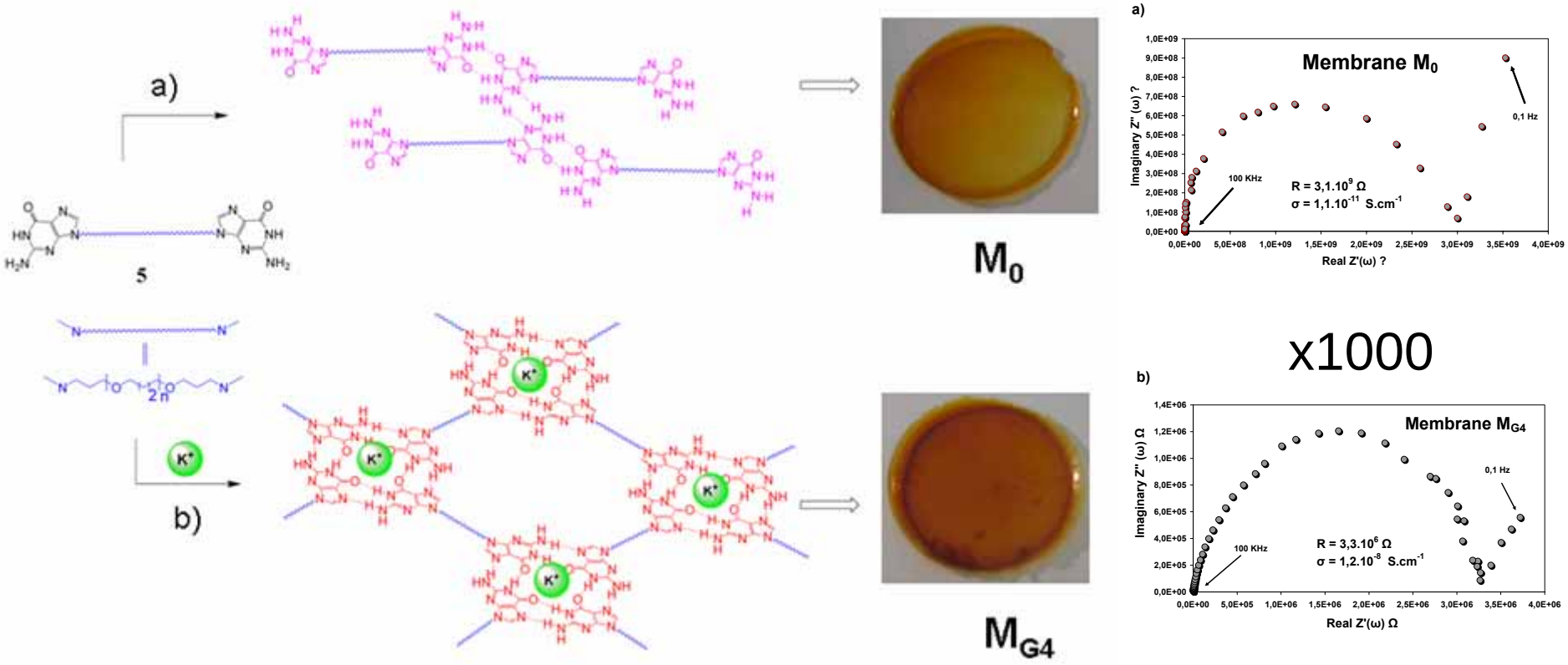
Angew. Chem. Int. Ed. **2007**, 46, 4268.

Functional G-Quartet Macroscopic Membrane Films

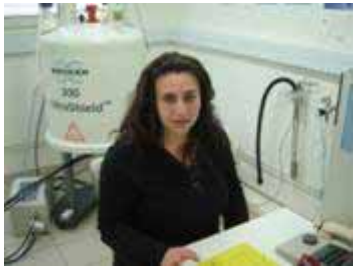


Angew. Chem. Int. Ed. **2007**, 46, 8409-8413.

Functional G-Quartet Macroscopic Membrane Films



Angew. Chem. Int. Ed. **2007**, 46, 8409-8413.



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