Journal Club

E. W. Meijer and cowokers, "Probing the Solvent-Assisted Nucleation Pathway in Chemical Self-assembly", Science **313**, 80 (2006)

4th Jul. 2015 Yoonnam Jeon

Probing the Solvent-Assisted Nucleation Pathway in Chemical Self-Assembly

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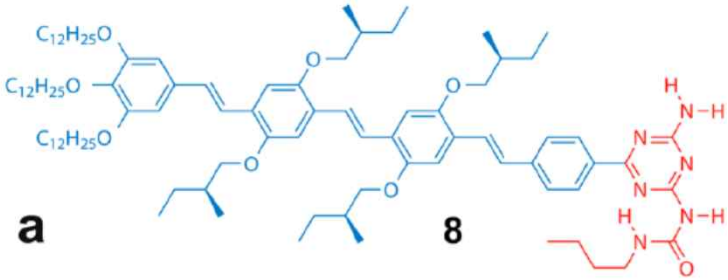
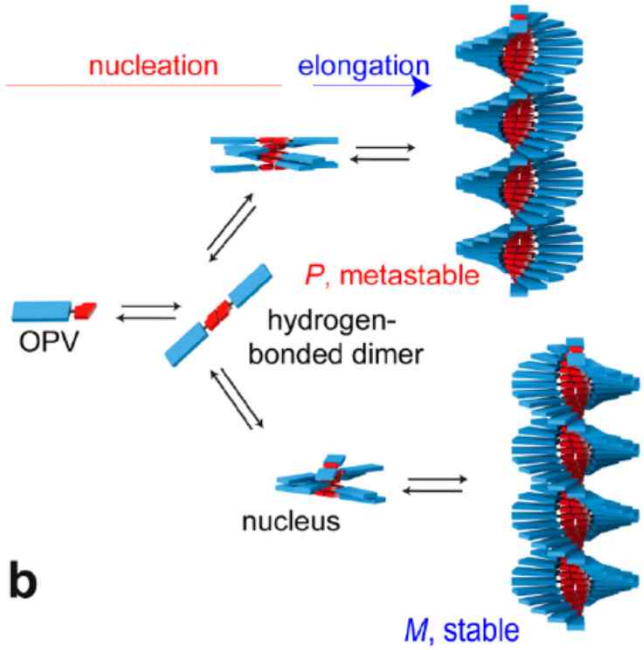
Hierarchical self-assembly offers a powerful strategy for producing molecular nanostructures. Although widely used, the mechanistic details of self-assembly processes are poorly understood. We spectroscopically monitored a nucleation process in the self-assembly of π-conjugated molecules into helical supramolecular fibrillar structures. The data support a nucleation-growth pathway that gives rise to a remarkably high degree of cooperativity. Furthermore, we characterize a helical transition in the nucleating species before growth. The self-assembly process depends strongly on solvent structure, suggesting that an organized shell of solvent molecules plays an explicit role in rigidifying the aggregates and guiding them toward further assembly into bundles and/or gels.

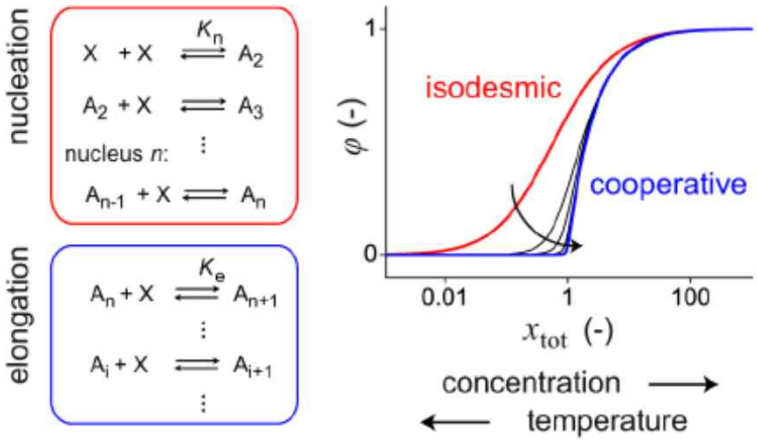
Soft-Matter Optical Spectroscopy

Overview





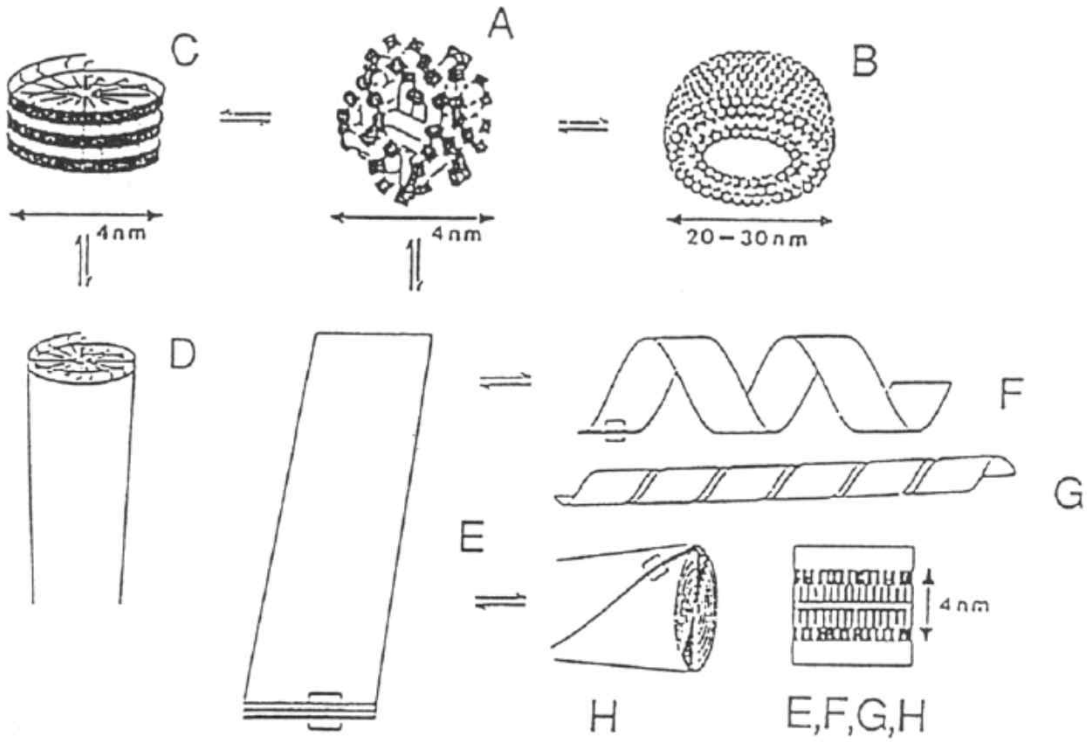
- Molecular interactions
- Characterizations
  - Dimer & Fibril structures
  - Thermodynamics & Models
  - Solvent effect
- Pathway control by Conc. & Temp.



Meijer and coworkers, *Chem. Mater.* **26**, 576 (2014)

Introduction - Issues of self-assembly

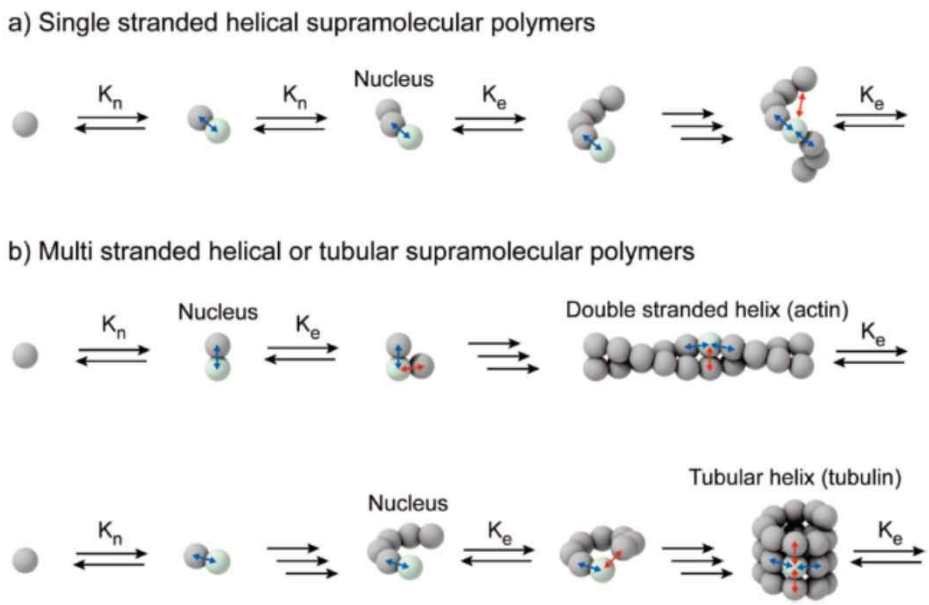
Geometry change & curvature energy Fuhrhop and Helfrich, *Chem. Rev.* **93**, 1565 (1993)



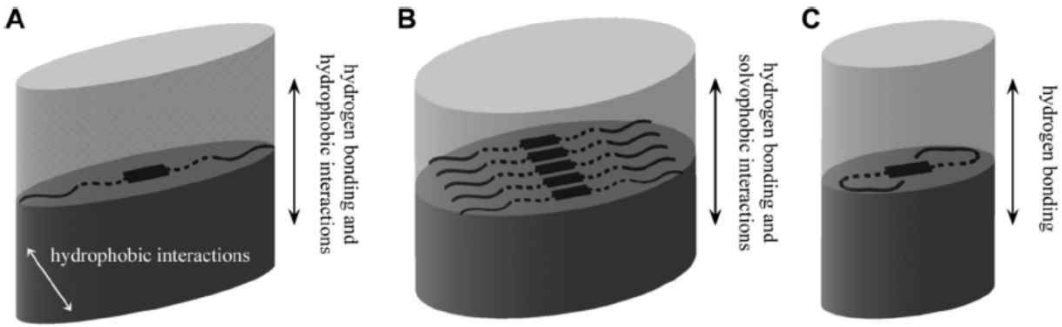
A (micelles) & B (Vesicles) : repulsive interactions of the head groups
C (Disk micelles) & D (bilayer rods)
E (Bilayer sheet) : strong binding interactions on the surface
F (helical ribbons), G & H (mono- & multilayer tubules)

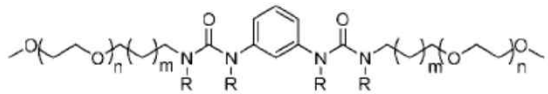
Introduction - Driving forces & Topology

Meijer and coworkers, *Chem. Rev.* **109**, 5687 (2009)



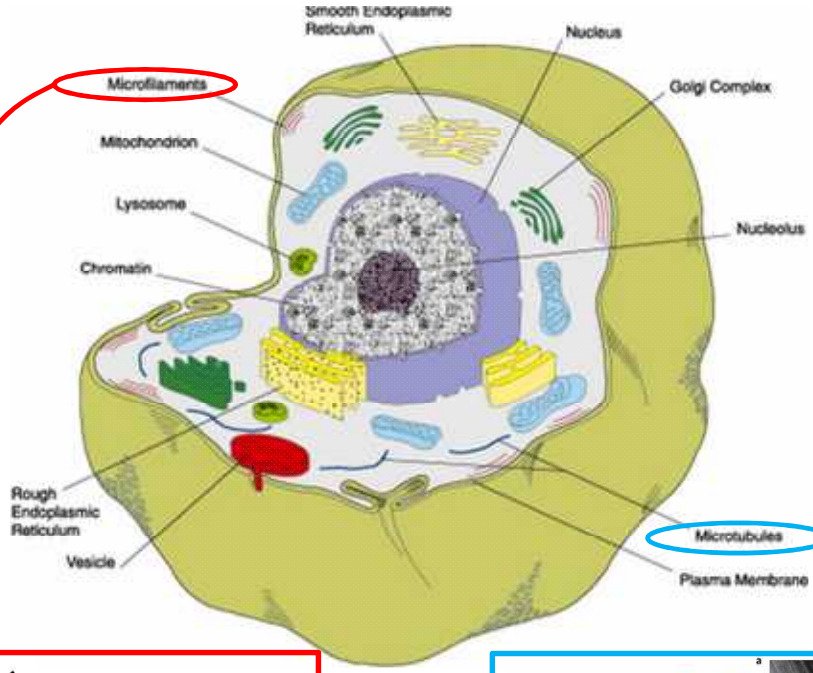
→ : secondary interactions responsible for the cooperative growth

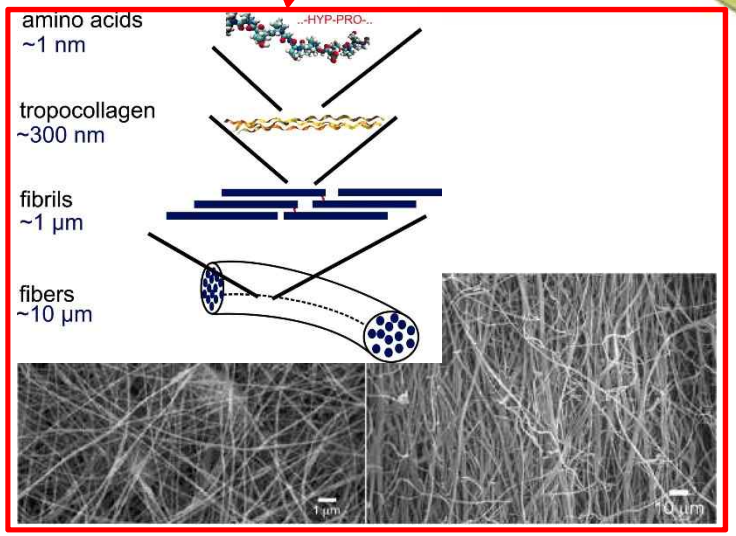


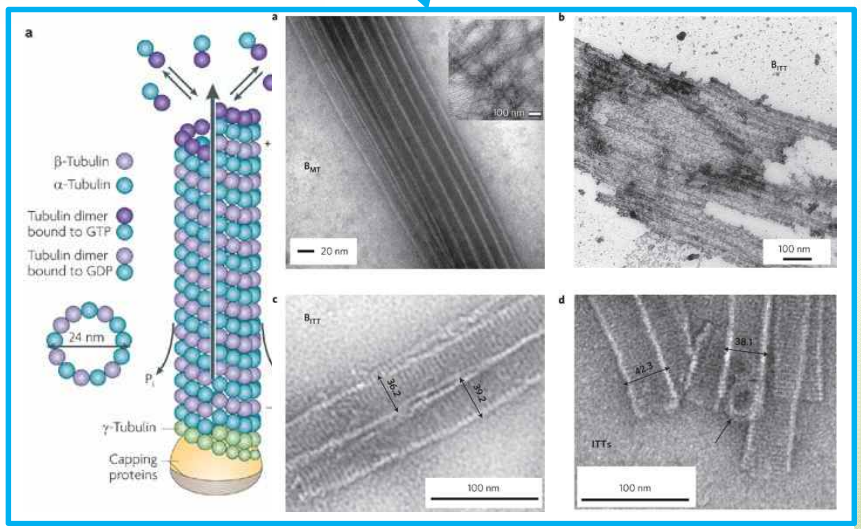


Driving forces present in
(A) water
(B) acetonitrile
(C) toluene

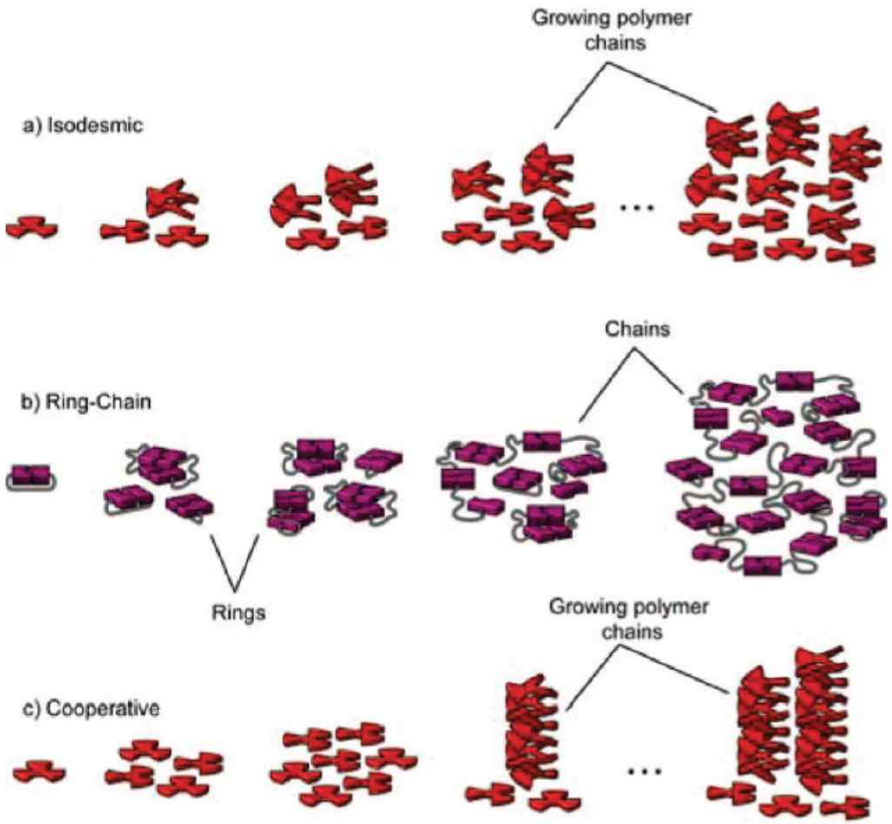
Introduction - Self-assembly of peptide amphiphiles







Introduction - Protein aggregation models

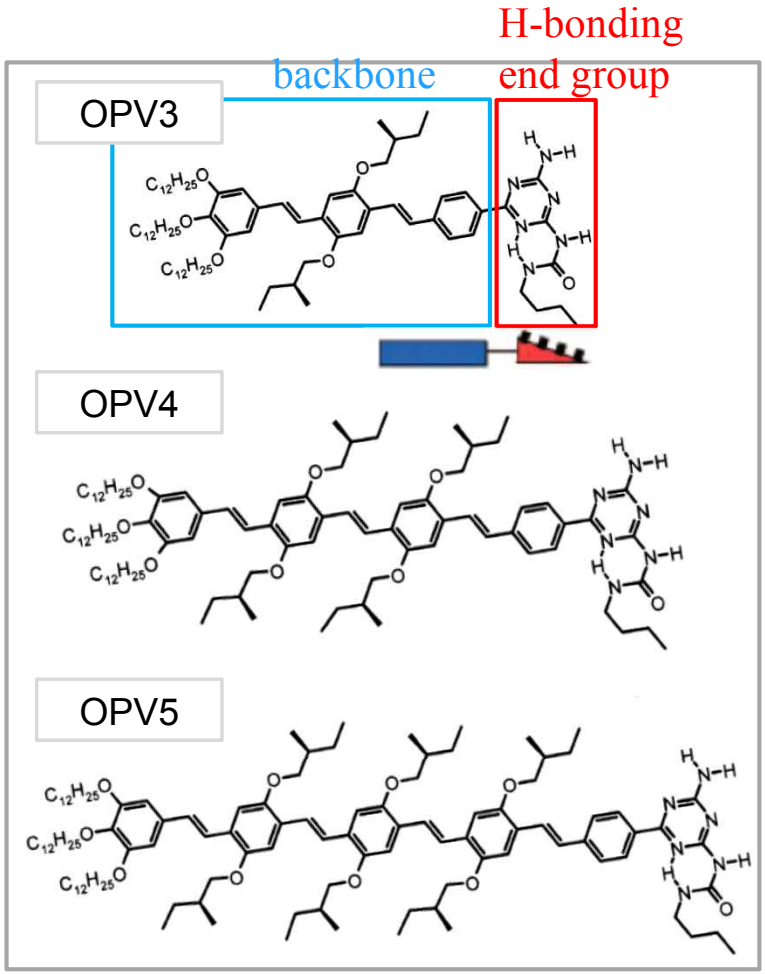


Meijer and coworkers, *Chem. Rev.* **109**, 5687 (2009)

Isodesmic model
(multistage open association model)
- Noncooperative
- Association constant is independent of the size of the object

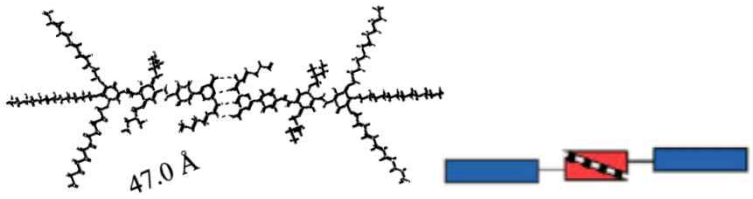
Nucleated self-assembly
(nucleation growth or initiation elongation)
- Cooperative kinetics
- size-dependent association constant

Samples - Oligo (*p*-phenylenevinylene) derivatives (OPV-*x*)



+ Chloroform (solvent)

- **Monomers & H-bonded dimers**



+ dodecane (solvent)

- **Helical stacks**

Meijer and coworkers, *J. Am. Chem. Soc.* **125**, 15941 (2003)

Characterizations - Aggregation in the dodecane solvent

Meijer and coworkers, *J. Am. Chem. Soc.* **125**, 15941 (2003)

UV/Vis & Fluorescence
- Red shift with decreasing Temp. : π–π* transitions

Circular dichroism
- **negative coupling** in cooling process : presence of a **left-handed helical arrangement** of the transition dipoles of the OPV molecules

	UV/vis (λ_{max} in nm)		PL ($\lambda_{em,max}$ in nm)		CD (g_{abs})	ΔH	ΔS
	$CHCl_3$	dodecane	$CHCl_3$	dodecane	dodecane	(kJ mol^{-1})	(J mol^{-1} K^{-1})
OPV3	412	411	470	478, 508	1.12×10^{-3}	−129.3	−334.9
OPV4	437	440	501	525, 550	1.89×10^{-3}	−161.4	−399.5
OPV5	444	453	515	561, 595	2.06×10^{-3}	−168.4	−405.7

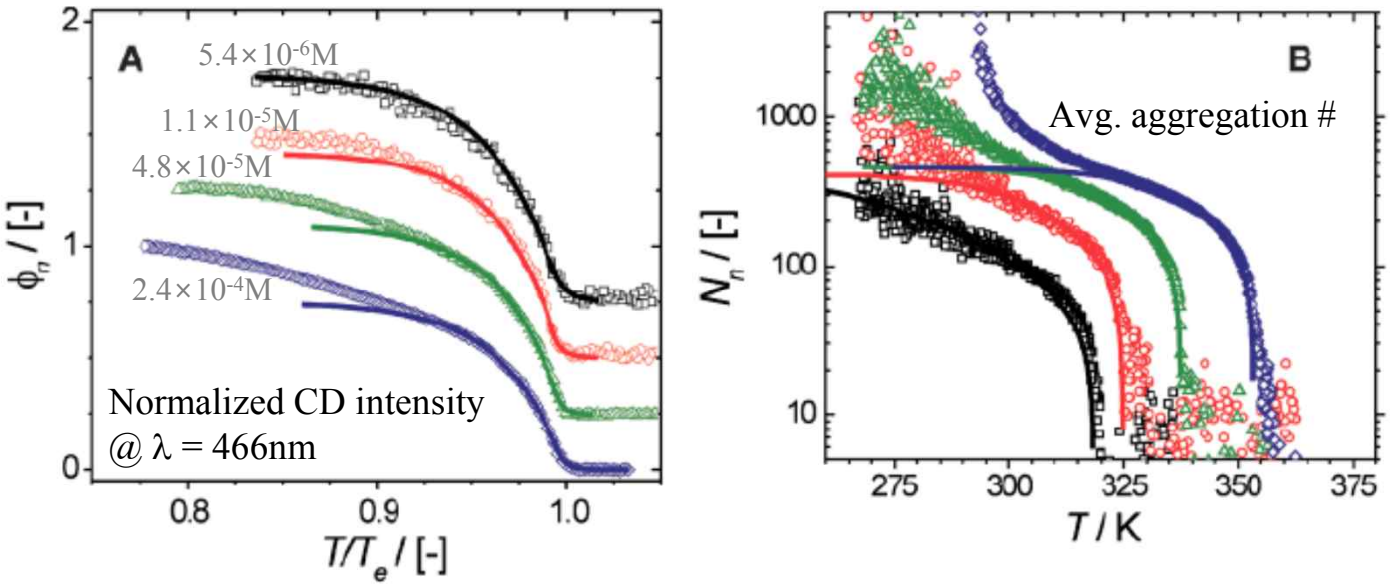
Enthalpy-driven process

SANS
- Model fitting with cylindrical structures

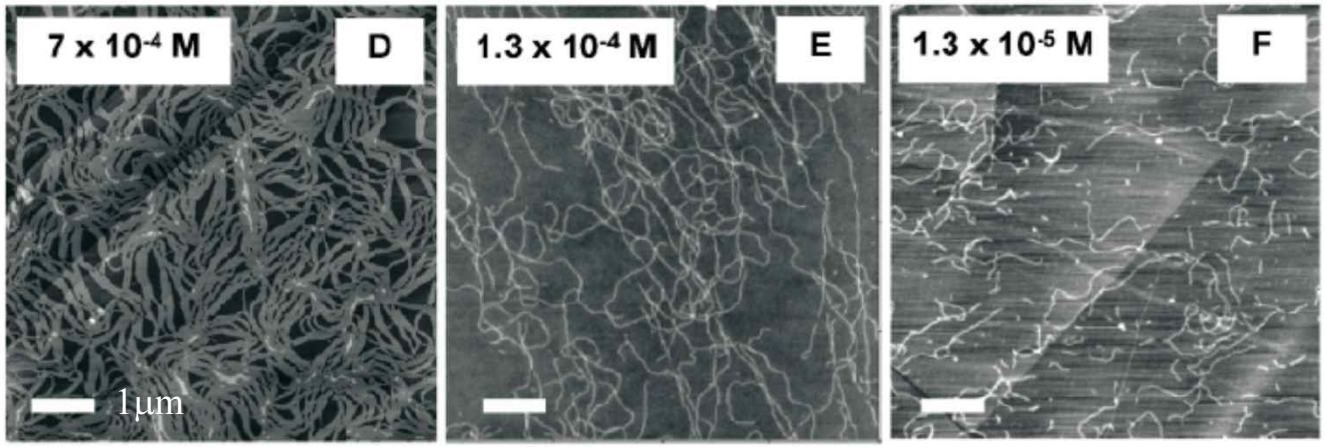
	OPV3	OPV4	OPV5
Length (nm)		150	
Diameter (nm)	5.0	5.8	

Characterizations - Aggregation in the dodecane solvent

OPV4 in dodecane upon cooling process

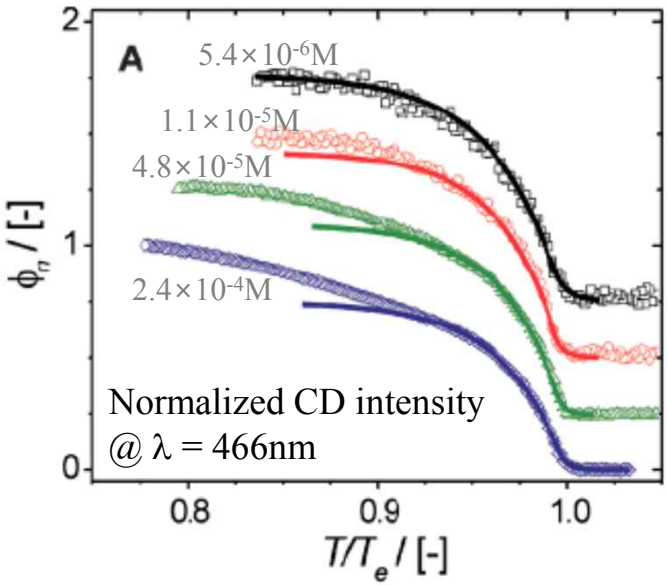


AFM images for OPV4 + dodecane drop cast on the graphite



Characterizations - Thermodynamic models

OPV4 in dodecane upon cooling process



Curve : not sigmoidal
→ cannot be described by an isodesmic model

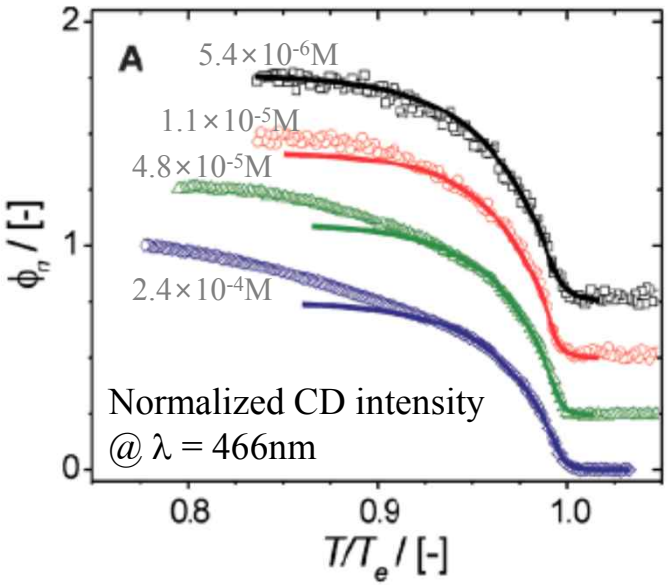
Introducing **Ising chain theory** : helix-coil transition

$$\phi_n \text{ (aggregation fraction)} = 1 - \exp[h_e(T-T_e)/RT_e^2] \qquad T < T_e$$
$$\sim K_a^{1/3} \exp[(2/3K_a^{-1/3} - 1)h_e(T-T_e)/RT_e^2 \qquad T \sim T_e$$

K_a : equilibrium constant of the activation step
h_e : molecular enthalpy of the elongation process
R : gas constant
T_e : polymerization temperature

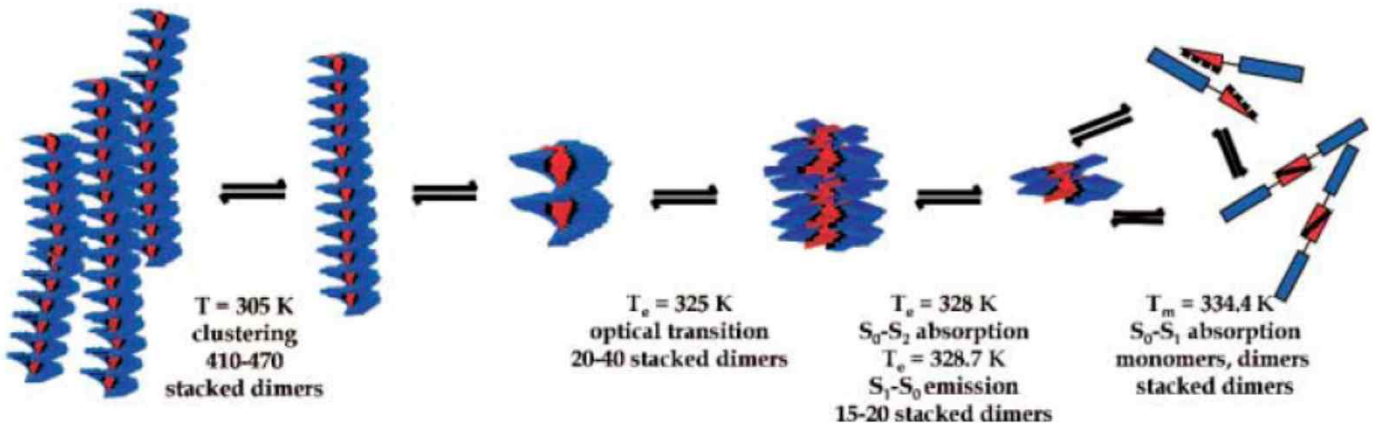
Characterizations - Thermodynamic models

OPV4 in dodecane upon cooling process



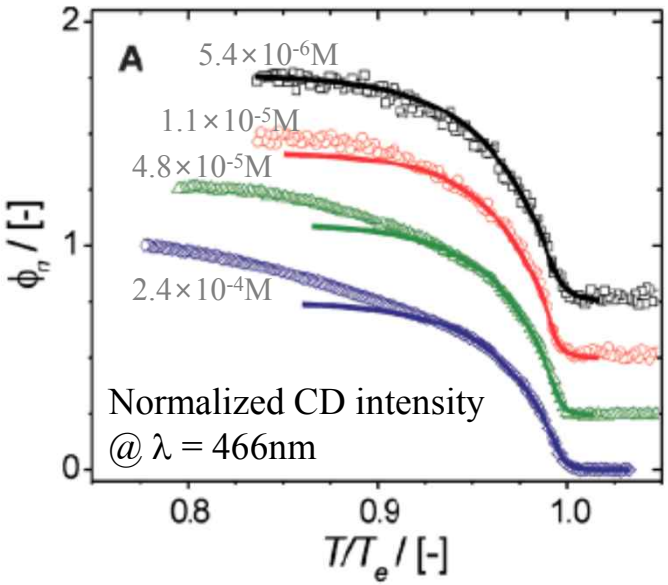
Fitting with Ising chain theory

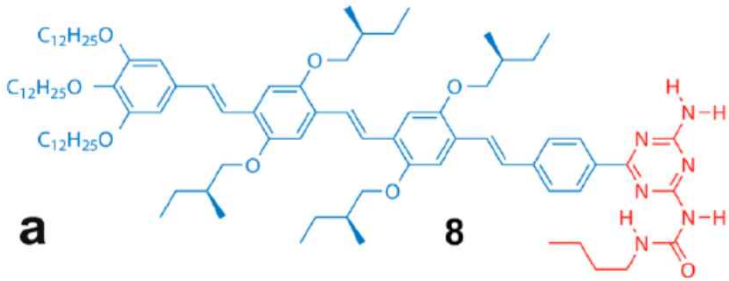
→ $T > T_e$: no helical aggregation

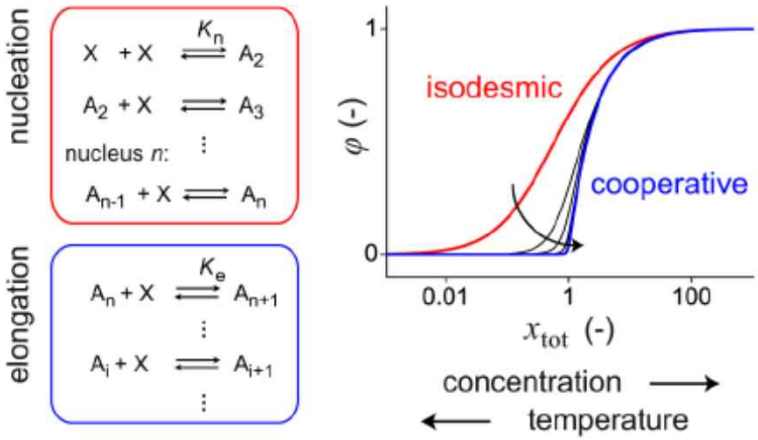


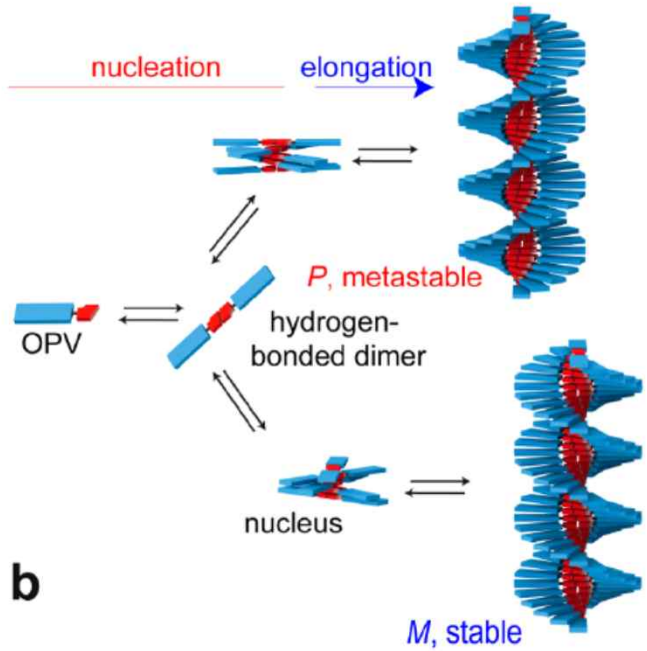
Pathway control - Temperature dependency

OPV4 in dodecane upon cooling process



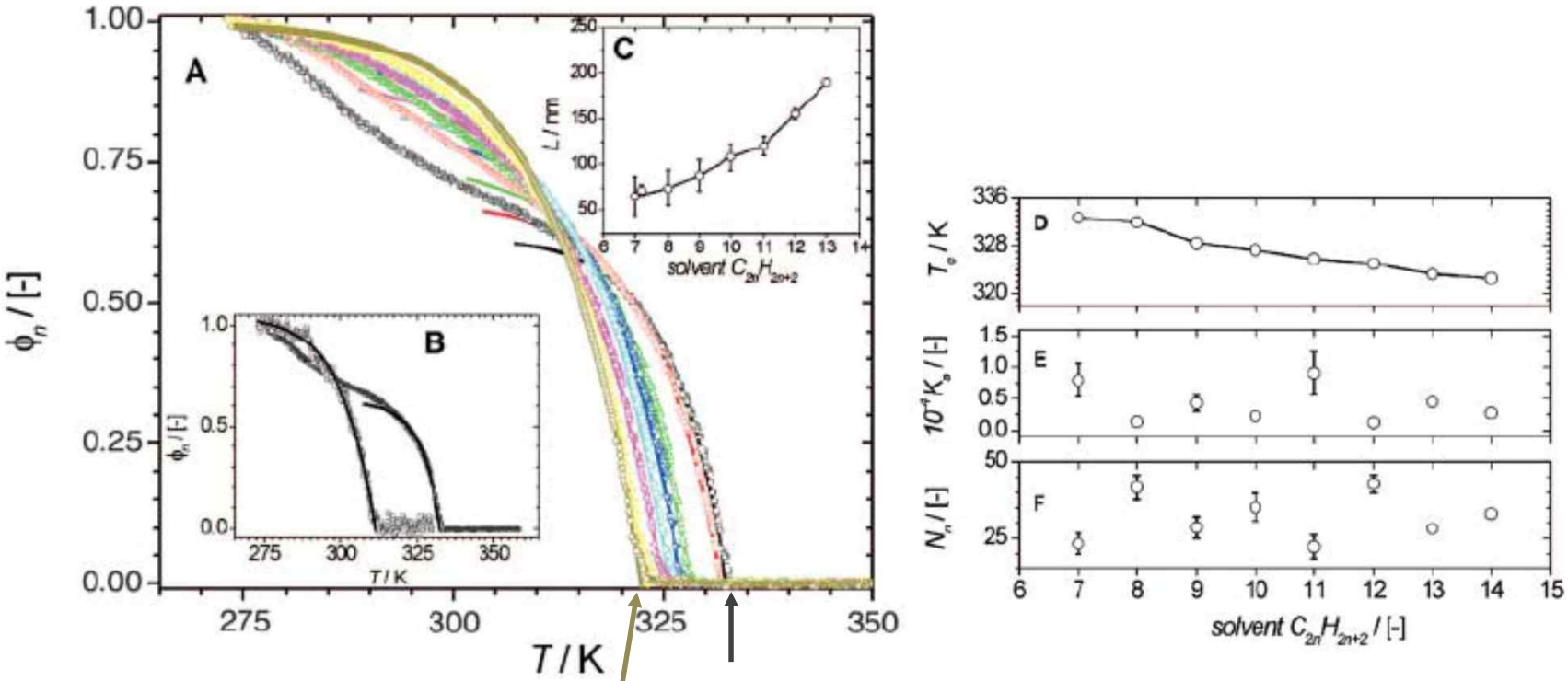






Meijer and coworkers, *Chem. Mater.* **26**, 576 (2014)

Role of solvent - Stability of the nuclei and stacks



T_e (heptane) = 332.7 K

T_e (tetradecane) = 322.5 K

Role of solvent in the assembly process :

Coorganization at the periphery of the aggregates