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1 and 2D Nanostructures suspensions: from discovery to applications

Jean-Christophe P. Gabriel

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Submitted on 14 Oct 2024

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1 and 2D Nanostructures suspensions: from discovery to applications

JEAN-CHRISTOPHE P. GABRIEL

JEAN-CHRISTOPHE.GABRIEL@CEA.FR

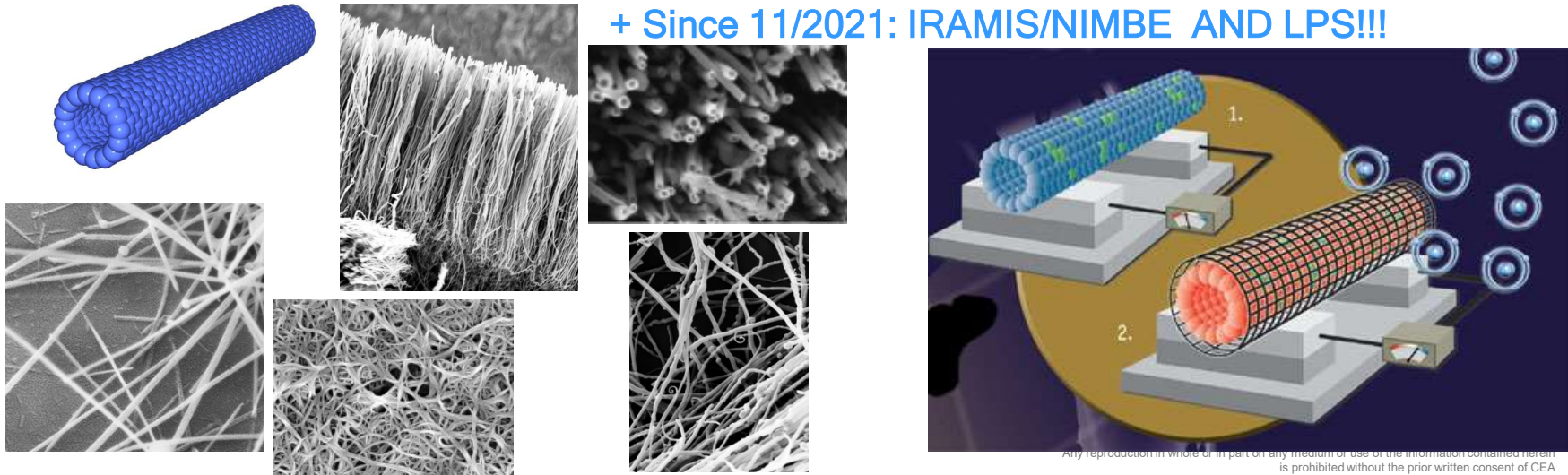


Happy 75th Patrick!

ChePhyMoSS 2023

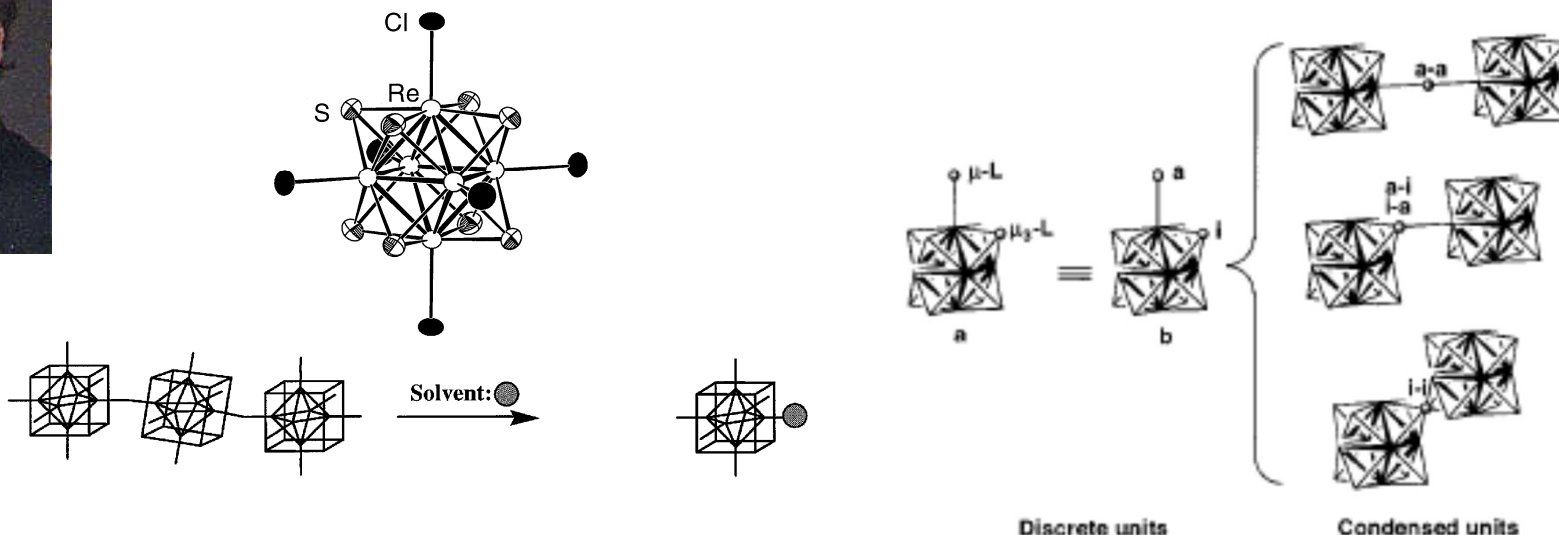
Curriculum's major items

- Ph. D. at LPS - Univ. Paris Saclay (Batail; Davidson) Molecular Chem
- Postdocs (1994-1995)
 - Nuclear Research Center, Risø, Denmark (K. Bechgaard) : 2D self assembly
 - 2y - Materials Research Laboratory, UCSB (A. K. Cheetham): Zeolites
- 4y @ CNRS, Institut Jean Rouxel, Nantes, France (Self assembly of nanowires & nanosheets) (1996-2001)
- 6y @ Nanomix: H₂ Storage & CNT integration - Chemical sensors ('01-'07)
- 14y @ CEA (DRT/LETI & DRF/PTNS) Since 01/2013 => co-PI ERC REECYCLE
Since 08/2018: @NTU Labo SCARCE : ewaste recycling (microfluidics/ScCO₂)
+ Since 11/2021: IRAMIS/NIMBE AND LPS!!!



From Solids to Chimie Douce: Patrick's Footprint

or How to Turn Rocks to Scientific Gold



Santiago Uriel Kamal Boubekeur

al. & Patrick Batail

Inorg. Chem. 32(13)2894-2900, 1993; *Acta Cryst.* C49, 1052-1056, 1993; *Bull. Soc. Chim. Fr.* 133, 783-794, 1996; *J. Chem. Soc., Chem. Commun.* 1998(7) 845-846, 1998; *C. R. Acad. Sci. IIC*, 1, 765-770, 1998; *Chem. Rev.* 101, 2037-2066, 2001

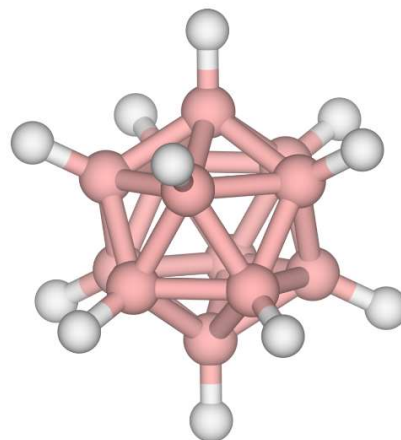
1989-1993: PhD Advisor => Defense, 24th Nov 1993! 30th anniv.

0D: Original CT Salts, beyond Re_6 : Icosaedra

α	$\text{B}_{12}\text{H}_{12}^{2-}$	$\text{CB}_{11}\text{H}_{12}^{-}$	$\text{CB}_{11}\text{H}_6\text{Br}_6^{-}$	$\text{B}_{12}\text{Br}_{12}^{2-}$	α
TTF α	Ref.: Kamal , FC1E, FC12E, DL1E. Structure ¹ : 3:1 α	FC3E α	α	Ref.: YB2E ·(BT2) [¶] ESR [¶] Structure ² : α	α
TMTTF α	YB5E, DL6E α	DL5E α	Ref.: YB3E-beta (à partir de la cellule à séchée). (Relancée: DL7E). [¶] Structure ³ : α	Ref.: YB4E [¶] Structure: 2 phases [¶] α ⁴ : 3·2·TBA: 2 [¶] ·RPE: 300·K, para. [¶] β ⁵ : 1:3·TBA: 2 α	α
BEDT-TTF α	Ref.: (FC4E)·FC4E- 4 [¶] Structure ⁶ : 2:2TCE: 1 α	FC5E α	Ref.: YB1E [¶] SQUID: Diamag.RX: Structure ⁷ : 2:2 α	α	α
EDT-TTF α	Ref.: DL3E-1 [¶] Structure ⁸ : maille α	FC6E, DL2E α	FC7E, FC11E, DL4E α	α	α



Electrocrystallisation



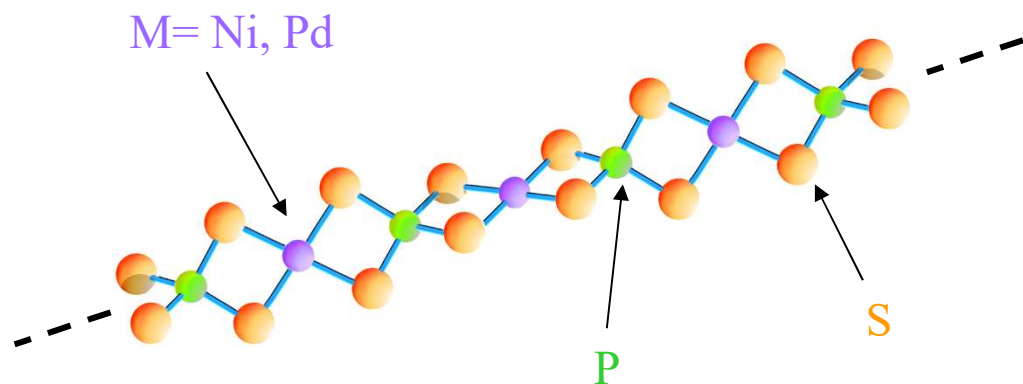
+ 1st synthesis C_{60} in France: Q4/1989

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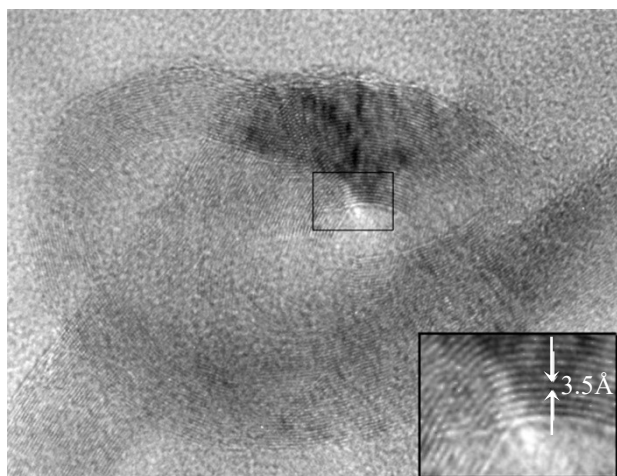
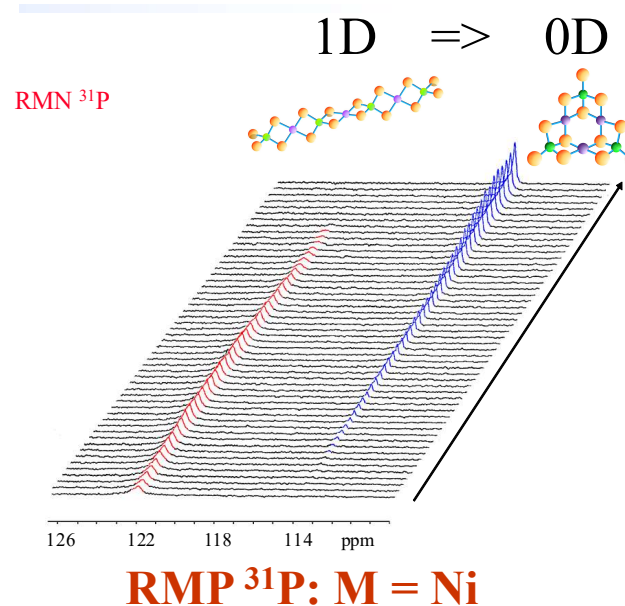
0D: Original CT Salts, beyond Re_6 : Icosaedra

1. Orthorhombique, : Etude préliminaire à 293K: $a=9.707(1)\text{Å}$, $b=10.378(2)$, $c=10.850$
2. Triclinique P-1:
 - 300K, refl.:
 - 150K, 5000 refl.: $a=13.2482(8)\text{Å}$, $b=16.0727(11)$, $c=16.0878(13)$, $\alpha=87.070(8)^\circ$, $\beta=89.215(7)$, $\gamma=88.709(7)$, $V=3420.0\text{Å}^3$.
3. Monoclinique, C2/c:
 - 300K, 446 refl.: $a=228.3513(60)\text{Å}$, $b=10.6406(22)$, $c=25.7556(50)$, $\beta=113.861(19)^\circ$, $V=7105.7\text{Å}^3$.
 - 150K, 5000 refl.: $a=28.0385(14)\text{Å}$, $b=10.5287(6)$, $c=25.7340(14)$, $\beta=114.178(5)^\circ$, $V=\text{Å}^3$.
4. Triclinique, P-1:
 - 300K, 570 refl.: $a=11.1125(33)\text{Å}$, $b=13.4057(41)$, $c=20.7297(60)$, $\alpha=72.974(30)^\circ$, $\beta=80.011(30)$, $\gamma=84.821(32)$, $V=2905\text{Å}^3$.
 - 150K, 5000 refl.: $a=11.0146(8)\text{Å}$, $b=20.4962(14)$, $c=26.6271(18)$, $\alpha=72.963(7)^\circ$, $\beta=84.556(7)$, $\gamma=78.573(7)$, $V=5629.1\text{Å}^3$.
5. Triclinique, P-1:
 - 300K, 246 refl.: $a=17.944(7)\text{Å}$, $b=17.972(6)$, $c=19.944(7)$, $\alpha=111.70(7)^\circ$, $\beta=111.75(3)$, $\gamma=91.66(4)$, $V=5447\text{Å}^3$.
 - Maille monoclinique I: $a=19.943(7)\text{Å}$, $b=25.763(6)$, $c=22.221(8)$, $\alpha=89.9^\circ$, $\beta=107.40(4)$, $\gamma=90.01$, $V=10894\text{Å}^3$.
 - 150K, 5000 refl.: $a=17.5869(13)\text{Å}$, $b=18.1182(12)$, $c=19.5930(13)$, $\alpha=113.420(6)^\circ$, $\beta=110.516(7)$, $\gamma=91.148(7)$, $V=5272\text{Å}^3$.
6. Triclinique, P-1:
 - 300K, 295 refl.: $a=8.6158(45)\text{Å}$, $b=11.2706(65)$, $c=12.7523(62)$, $\alpha=74.379(57)^\circ$, $\beta=85.734(54)$, $\gamma=81.677(59)$, $V=\text{Å}^3$.
 - 150K, 3679 refl.: $a=8.4974(9)\text{Å}$, $b=11.1429(13)$, $c=12.7696(14)$, $\alpha=74.453(11)^\circ$, $\beta=86.633(11)$, $\gamma=82.469(12)$, $V=1154.5\text{Å}^3$.
7. Monoclinique, P2₁/c: 150K, 5000 refl.: $a=9.6384(10)\text{Å}$, $b=17.6932(14)$, $c=18.3034(20)$, $\beta=101.633(11)$, $V=3057.2\text{Å}^3$.
8. Monoclinique, :
 - 300K, refl.: $a=()\text{Å}$, $b=()$, $c=()$, $\alpha=()^\circ$, $\beta=()$, $\gamma=()$, $V=\text{Å}^3$.
 - 150K, 5000 refl.: $a=()\text{Å}$, $b=()$, $c=()$, $\alpha=()^\circ$, $\beta=()$, $\gamma=()$, $V=\text{Å}^3$.

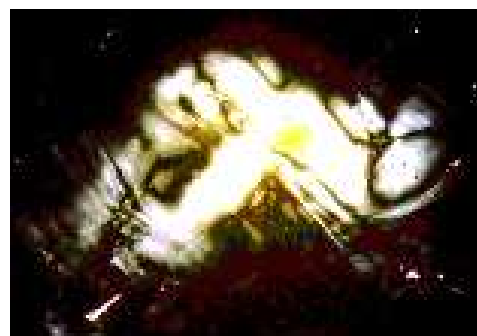
From Molecular to 1D: Flexible



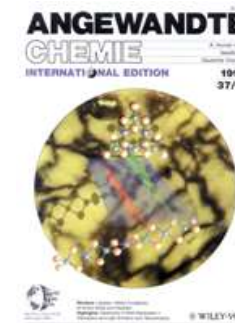
KMPS₄: Chain based on [MS₄] squares and [PS₄] tetrahedra



TEM image of dried solutions



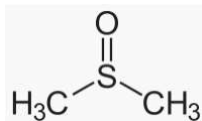
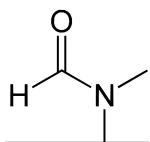
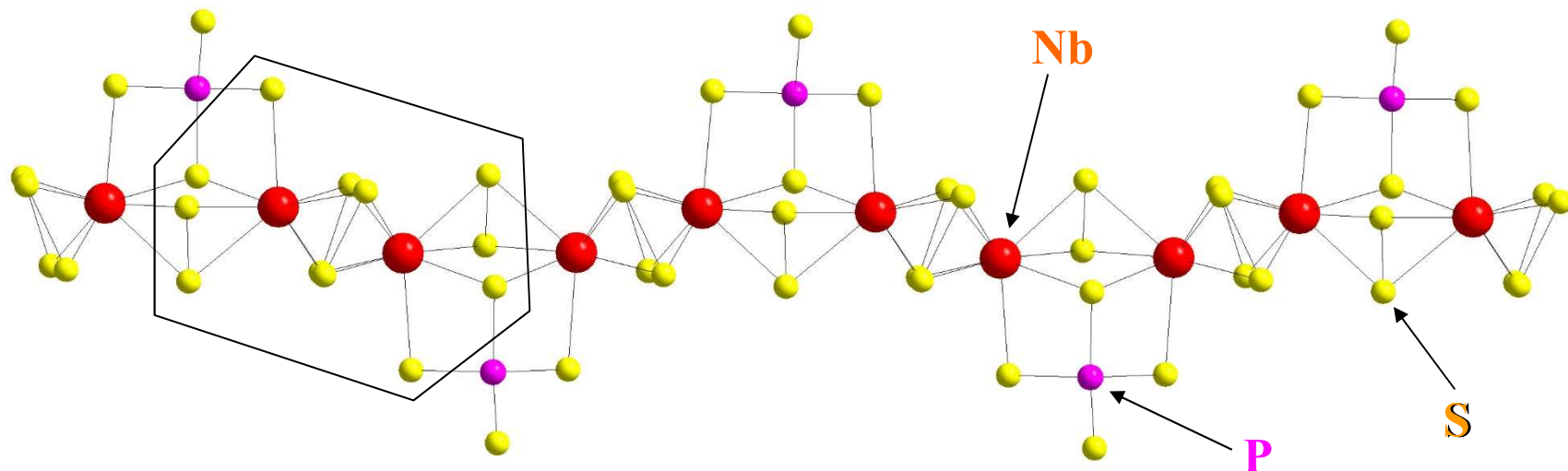
KPdPS₄/DMF : Transient textures



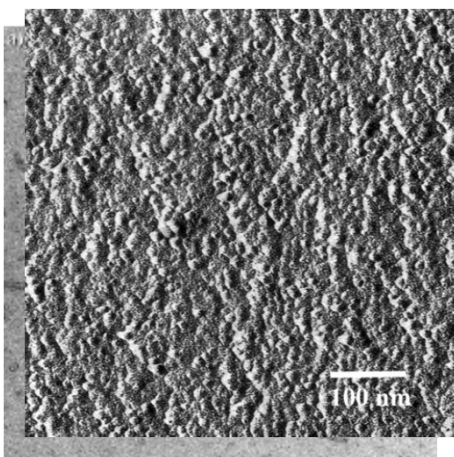
al. et Batail Angew. Chem. Int. Ed. 37(12) 1711-1714, 1998

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1D: From Flexible to Rigid + H Bonds

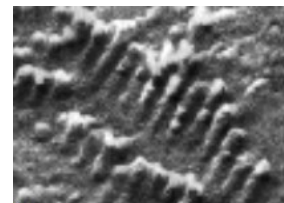


■ In DMF and DMSO, $\infty^1[\text{Nb}_2\text{PS}_{10}]^-$ chains are flexible and behave similarly to $\infty^1[\text{MPS}_4]^-$ (M = Ni, Pd) in solution (3D swelling, globular)



■ In NMF or FA = Strong H bond donors: a structuration of the polymer into SWNTs is observed (made of hydrogen bond stabilized helix, pitch = 7 nm).

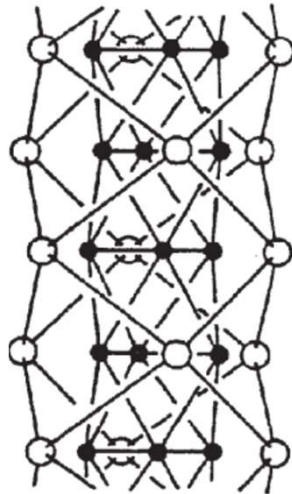
■ These nanotubes can aggregate into hexagonal bundles that can be melted by shearing



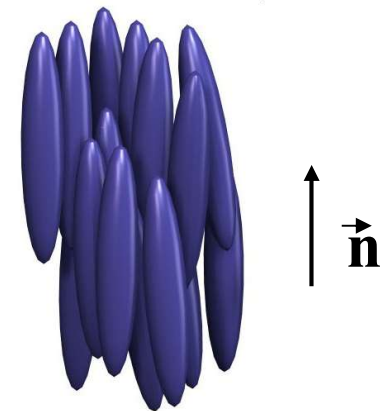
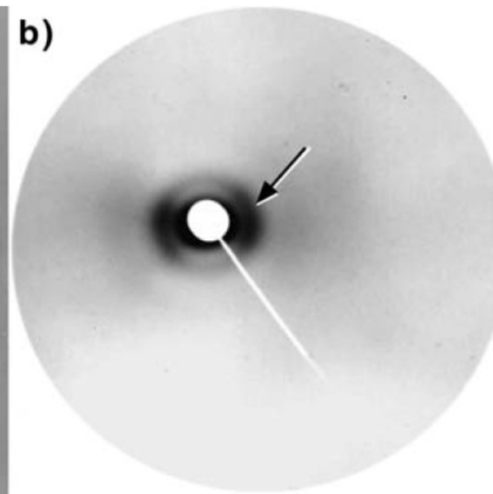
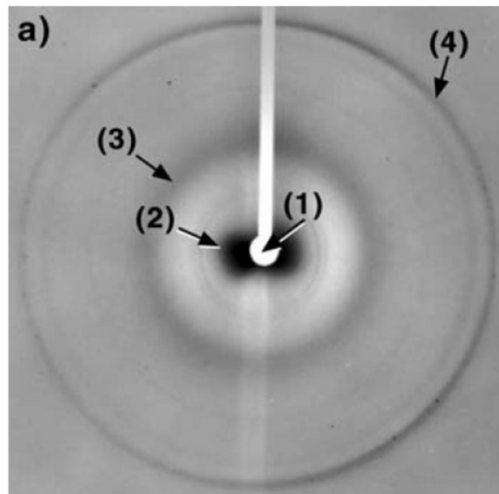
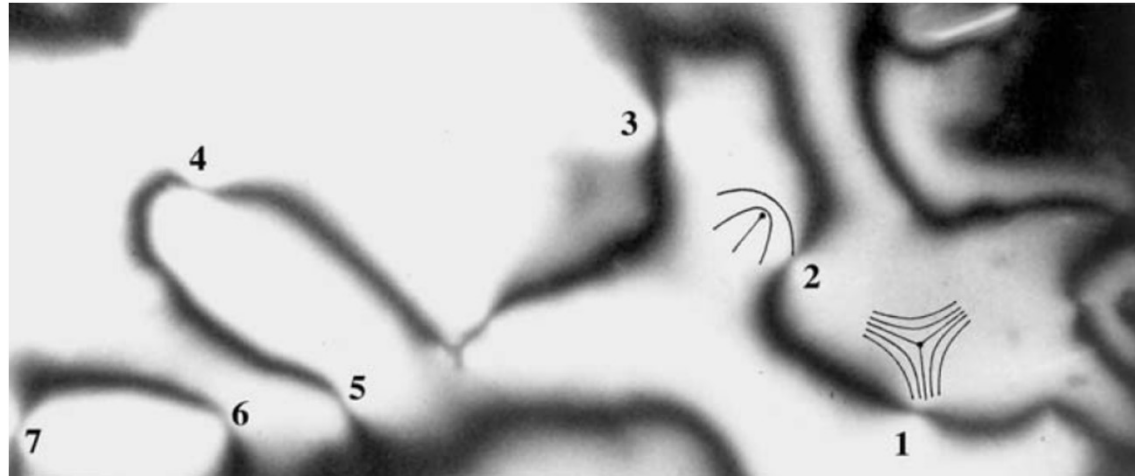
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al. et Batail Nanoletters 2(4) 403-407 (2002)

1D Rigid: The I-N Phase transition



Optical Microscopy, polarisers crossed



Davidson, Gabriel, Levelut, **Batail** *Adv. Mater.* 5(9)665 (1993)

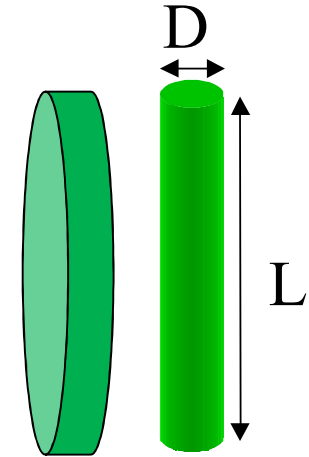
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Onsager Model (1949) for Nematic/Isotropic transition

For Molecules:

- **Rigid**
- **Anisotropic (batons ou disques)**

Only consider hard core interactions =>
1st order transition I – N, *athermal*.



$$c = L/D \cdot \phi$$

Φ : fraction volumique de particules

At transition, there is phase separation with

$$c_{\text{iso}}=3,3; c_{\text{ném}}=4,2 \text{ et } S = 0,80$$



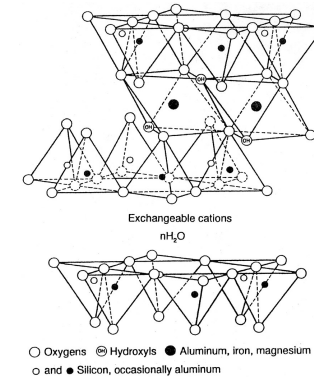
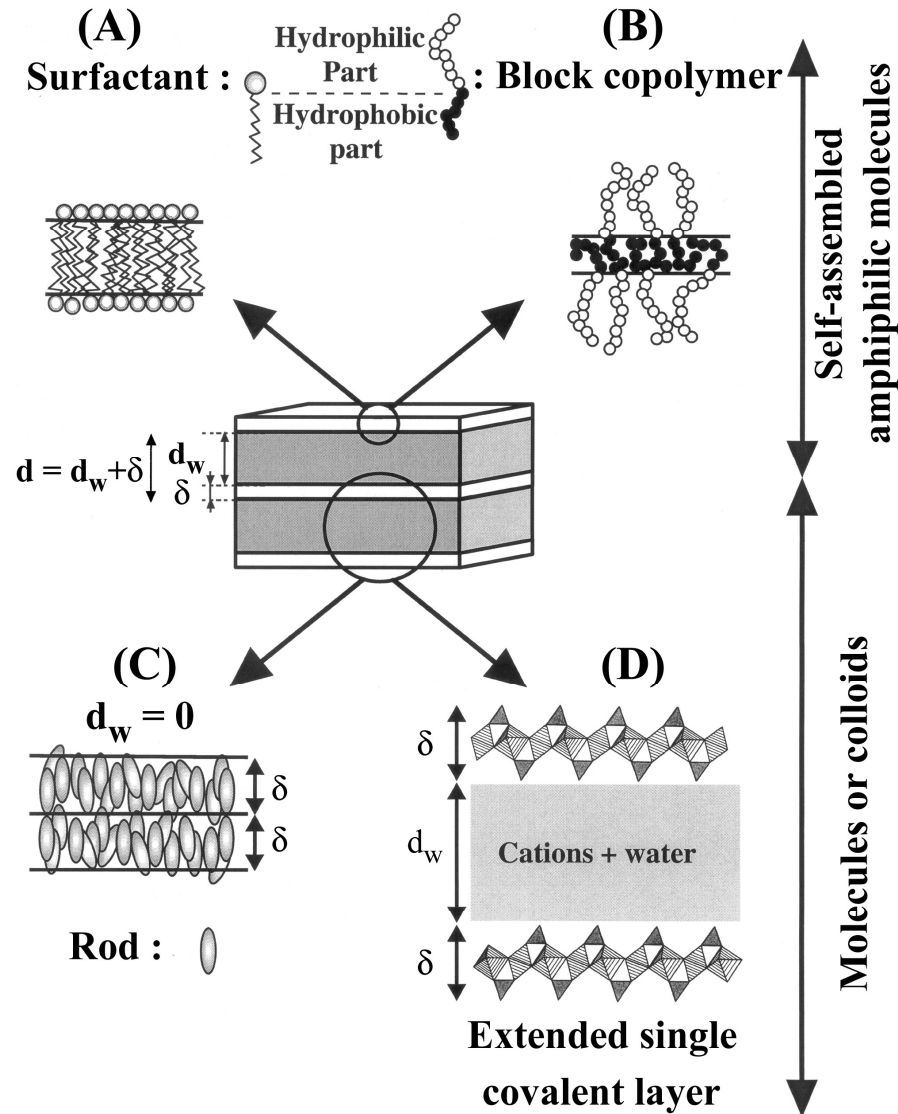
Anne-Marie Levelut

1937-2023

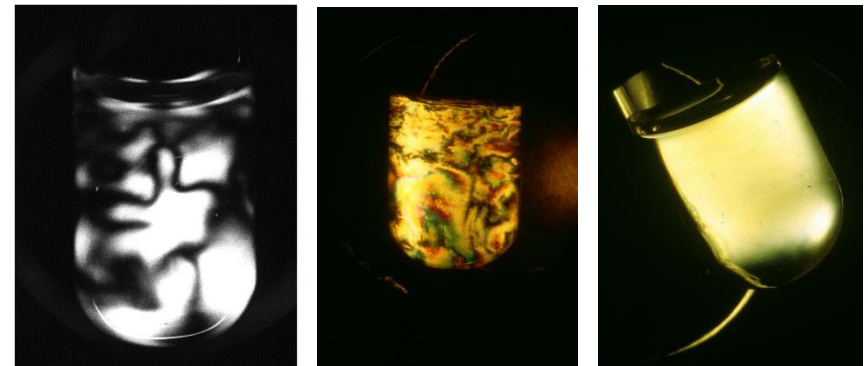
Acad. Sci., 1949, 51, 627; b) G. J. Vroege, H. N. W. Lekkerkerker, *Rep. Prog. Phys.*, 1992, 55, 1241.

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Quid 2D Nanosheets? Smectic Phase?



Smectite (!) Clays



Another Nematic BUT

=> The end of the house of card model

Gabriel *et al.* *J. Phys. Chem.* (1997) (320 cit.)

Lemaire *et al.* *Europhys. Lett.* (2002)

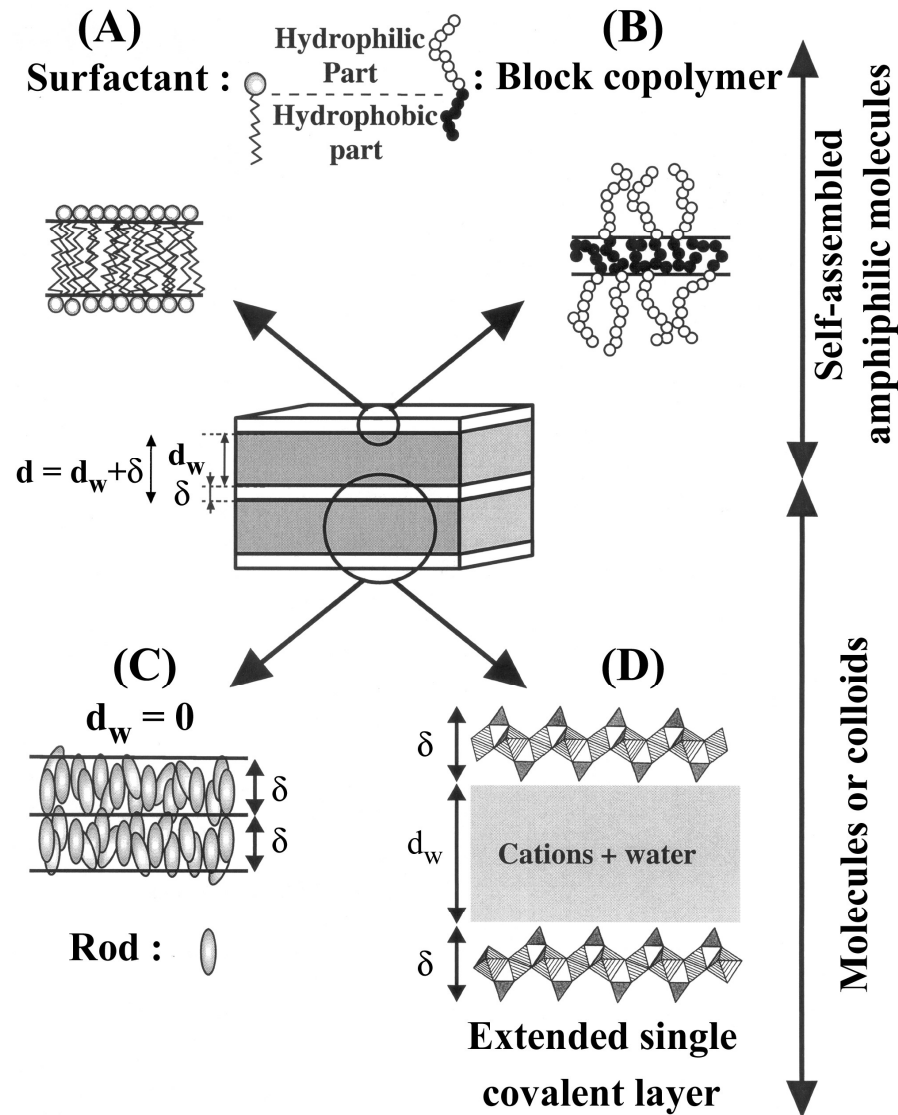
Davidson, Gabriel *Clay Sc.* (2005)

Paineau *et al.* *Liq. Cryst. Rev.* (2013)

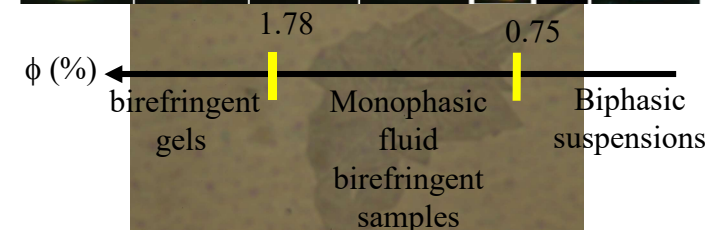
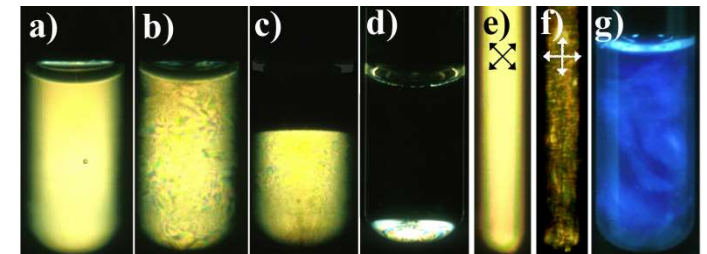
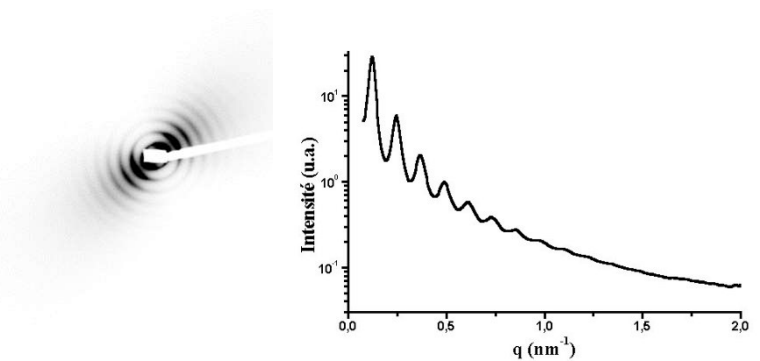
K. El Rifaii *et al.* *Langmuir* (2020)

No life as we know it without lamellar phases!

2D Nanosheets, Toward a Smectic Phase?



=> Cf presentation Patrick Davidson



Gabriel, Camerel, ... Davidson, **Batail**

Nature 413, 504 (2001)

Davidson et al. PNAS 2018

El Rifaii, Soft Matter 2021

Cherni et la. Nanoscale 2023



Applications?

**What to do with
nanostuctures?**

Enhanced NMR: Residual Dipolar Coupling

letters to nature

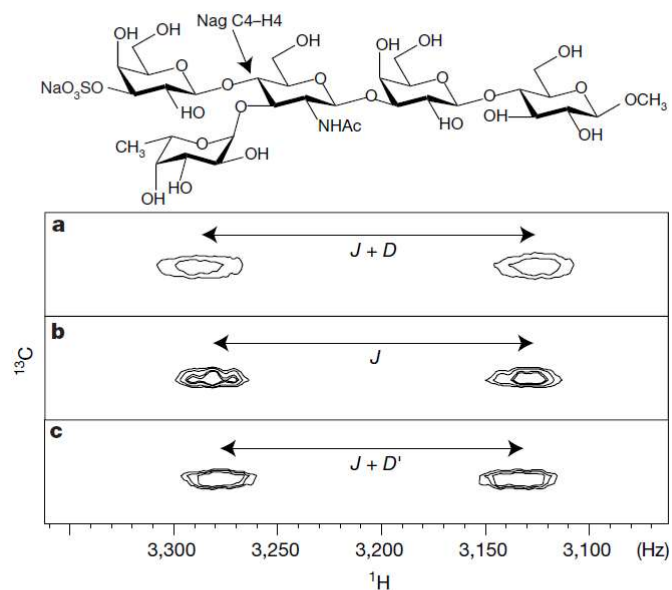


Figure 6 Superposition of three non-decoupled ^{13}C - ^1H NMR sub-spectra²⁹ of the glucosamine (Nag) C4-H4 region of the pentasaccharide containing the Lewis^x motif acquired in a suspension of V_2O_5 (**a**), in isotropic D_2O solution (**b**) and in a suspension of $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_4$ in D_2O , $\phi = 0.75\%$ (**c**). In **a** and **c**, the residual dipolar coupling $D = 15.7\text{ Hz}$ and $D' = -5.2\text{ Hz}$ superimposes to the scalar J coupling, confirming the induced alignment of the biomolecule. The different D values obtained using these two media illustrate the different induced alignments (see Supplementary Information).

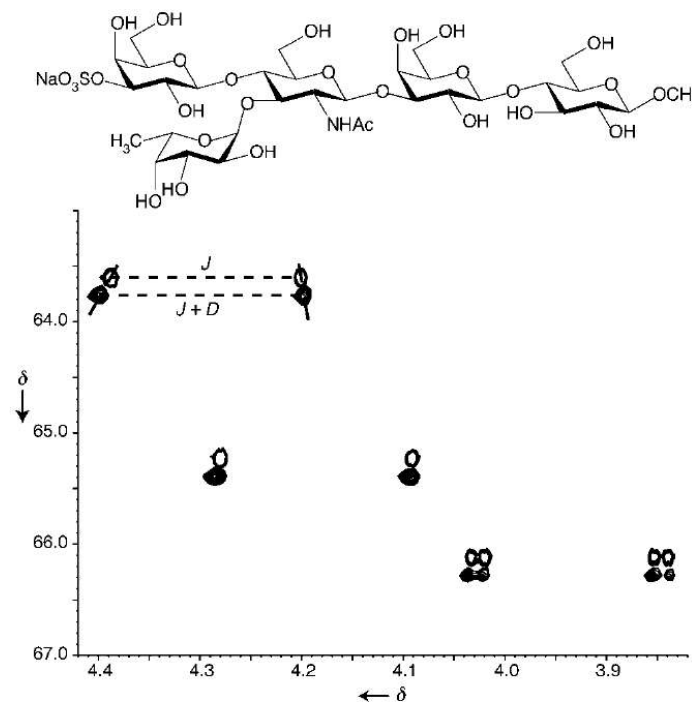


Figure 1. Overlay of a region of the ^{13}C - ^1H correlation maps of the pentasaccharide acquired in pure D_2O (light cross-peaks; this spectrum is shifted along the ^{13}C dimension by 0.15 ppm for clarity) and in the MLC medium (dark cross-peaks). Since no decoupling is applied during the acquisition time, the D values can be extracted. For the three C-H pairs shown, which correspond to the C4 of the sulfated galactose unit, the C4 of the galactose unit, and the C3 of the fucose unit (from top left to bottom right), the D values are equal to 8.3, 2.0, and -0.4 Hz , respectively.

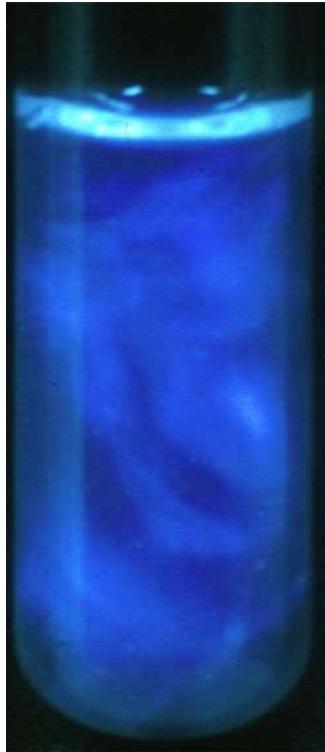
al. et Batail Nature 2001 (V_2O_5 & $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$)

al. et Batail. Angew. Chem. Int. Ed. 2001, 40(2) 373 (V_2O_5)

Berthault et al. *Carbohydrate Research* 338 (2003) 1771/1785 ($\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$ & V_2O_5)

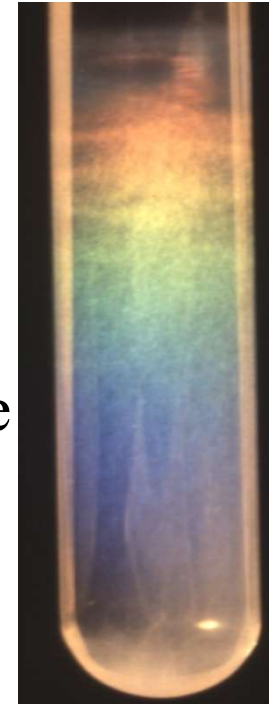
Application from Beautiful Science?

Sample iridescence observed in natural light



... due to light scattering by the $H_3Sb_3P_2O_{14}$ layers stacked with a period of 225 nm ($\phi = 0.75\%$)

Color tuned by separation between layers within a narrow volume fraction (ϕ) range



(12) **United States Patent**
Blackstock

(10) **Patent No.:** **US 7,334,910 B1**
(45) **Date of Patent:** ***Feb. 26, 2008**

(54) **DECORATIVE OPTICAL DISPLAY**

(76) Inventor: **Robert K. Blackstock**, 5699 Kanan Rd., #128, Agoura Hills, CA (US) 91301

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **11/490,752**

(22) Filed: **Jul. 20, 2006**

4,742,439 A * 5/1988 Choate 362/311
5,150,257 A * 9/1992 Mohabbatzadeh et al. . 359/601
5,683,174 A * 11/1997 Lena, Jr. 362/318
6,630,968 B1 * 10/2003 Tsuchihashi et al. 349/65
6,681,508 B2 * 1/2004 Unger et al. 40/406
7,019,810 B2 * 3/2006 Hubby, Jr. 349/159
2006/0133064 A1 * 6/2006 Lin 362/101

* cited by examiner

Primary Examiner—Sandra O'Shea

Assistant Examiner—Mary Zettl

(74) Attorney, Agent, or Firm—Koppel, Patrick, Heybl & Dawson; Michael J. Ram

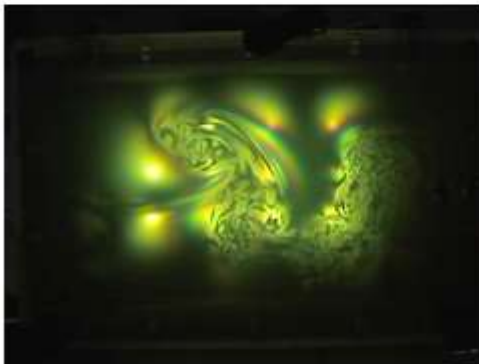
Vermiculite clay

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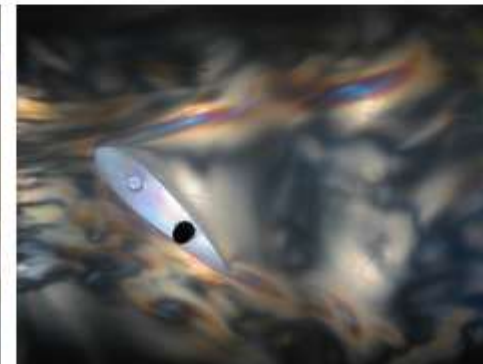
Vortex shedding



Vortex street



Flow separation

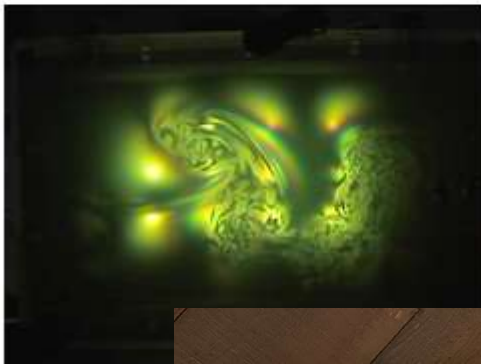


- Laminar has developed a compelling flow visualization fluid.
- This fluid spontaneously produces very colorful flow images.
- Go to the "[Downloads](#)" page to see videos and photos.
- This site and company are very much in early stages of development. As such, come back often to see new developments.

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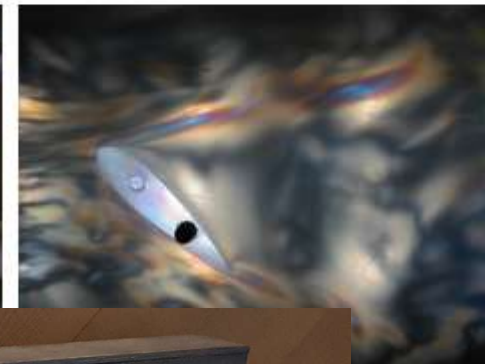
Vortex shedding



Vortex street



Flow separation



- Laminar
- This f
- Go to
- This s
such,

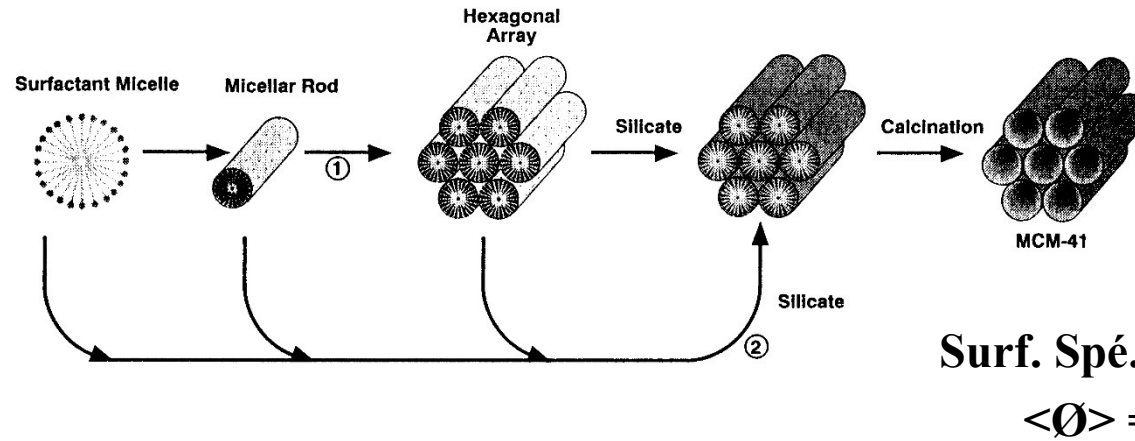


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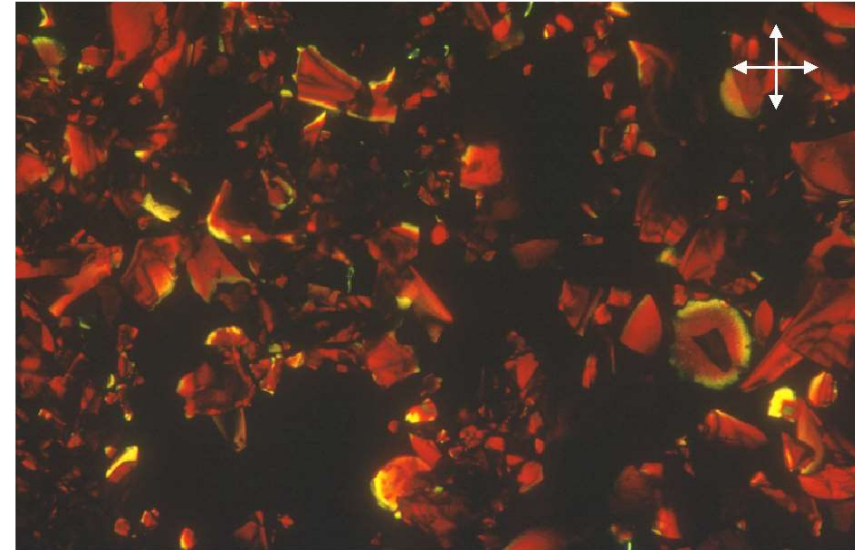
Lawrence Hall of Science, Berkeley, CA

MLCs' Applications : New Materials?

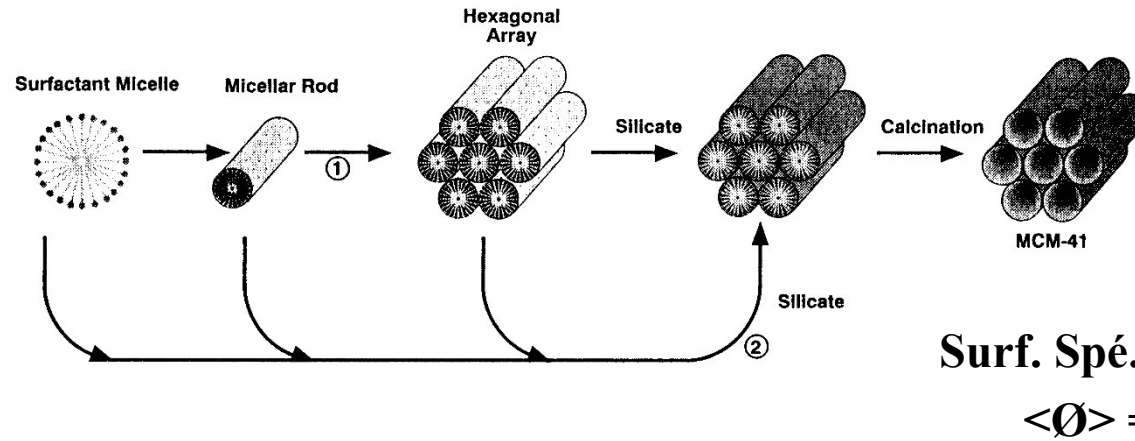


Synthesis in acidic conditions
with neutral or low charge
density precursors

Synthesis by polycondensation
of TEOS or TMOS within a
colloidal suspension of Nematic
V₂O₅, n H₂O

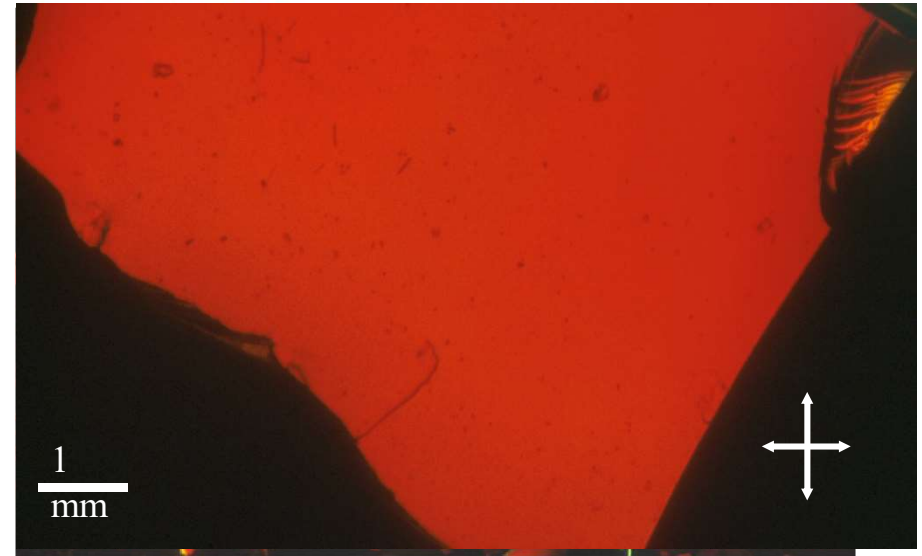


MLCs' Applications : New Materials?

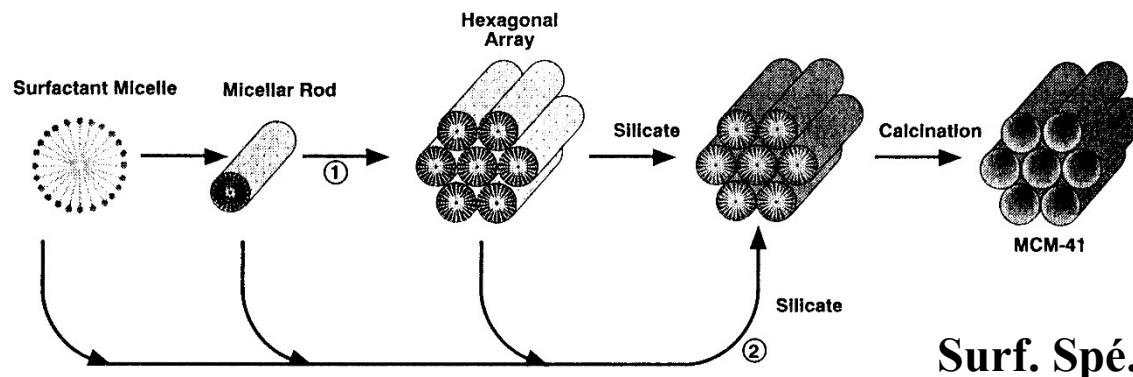


Synthesis in acidic conditions with neutral or low charge density precursors

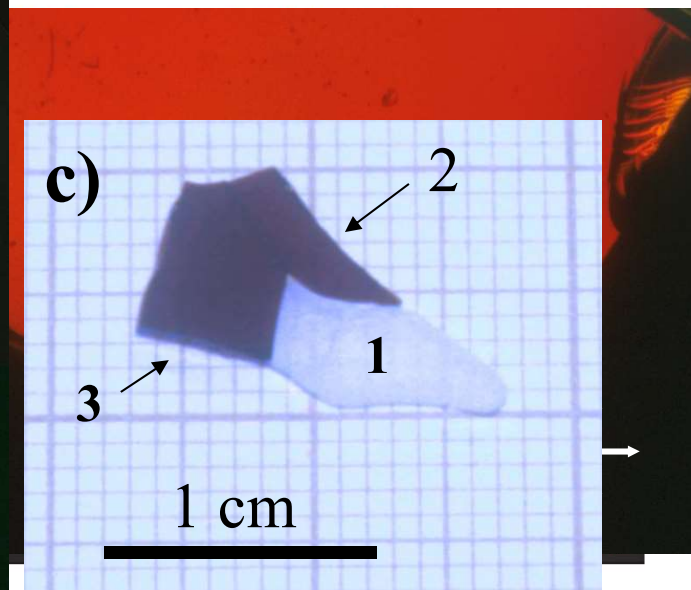
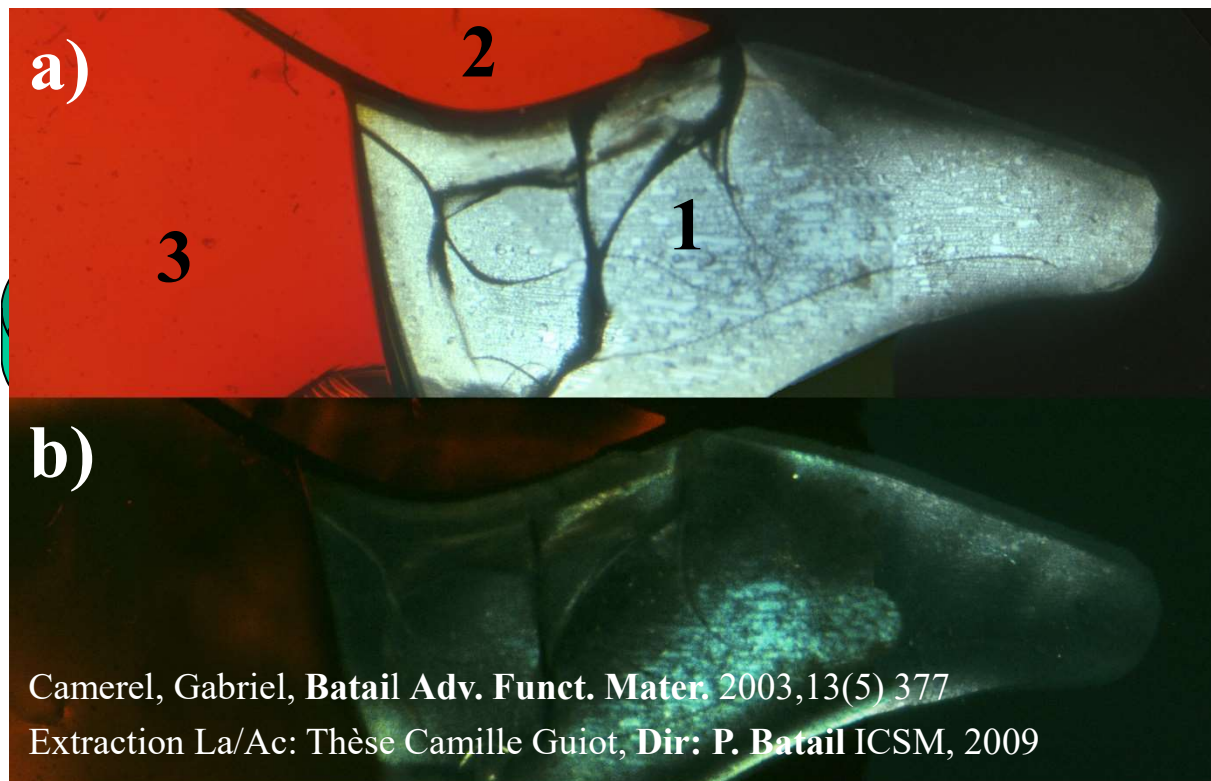
Synthesis by polycondensation of TEOS or TMOS within a colloidal suspension of Nematic V₂O₅, n H₂O



MLCs' Applications : New Materials?



Surf. Spé. = 207 m²/g
 $\langle \text{Ø} \rangle = 137 \text{ \AA}$

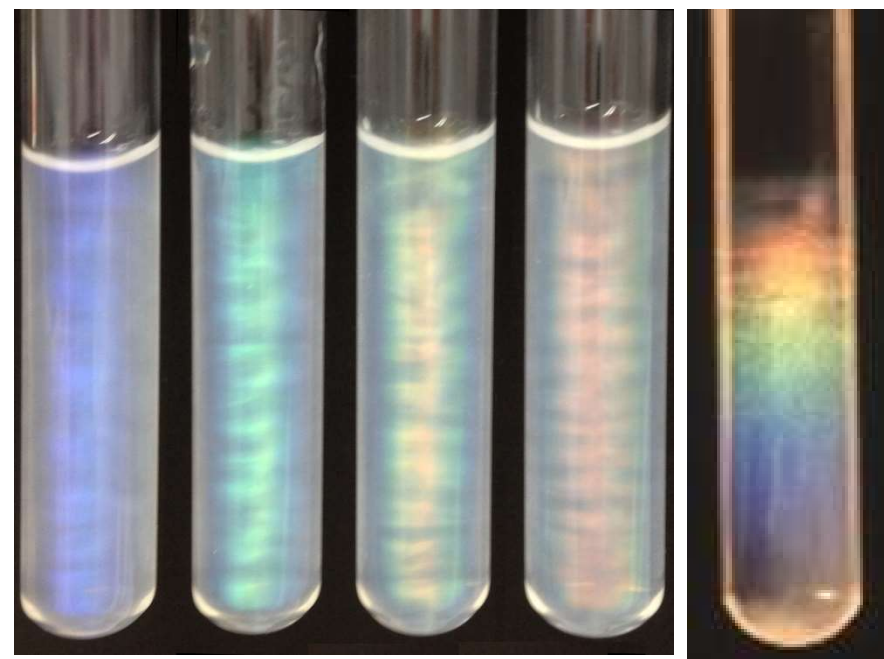
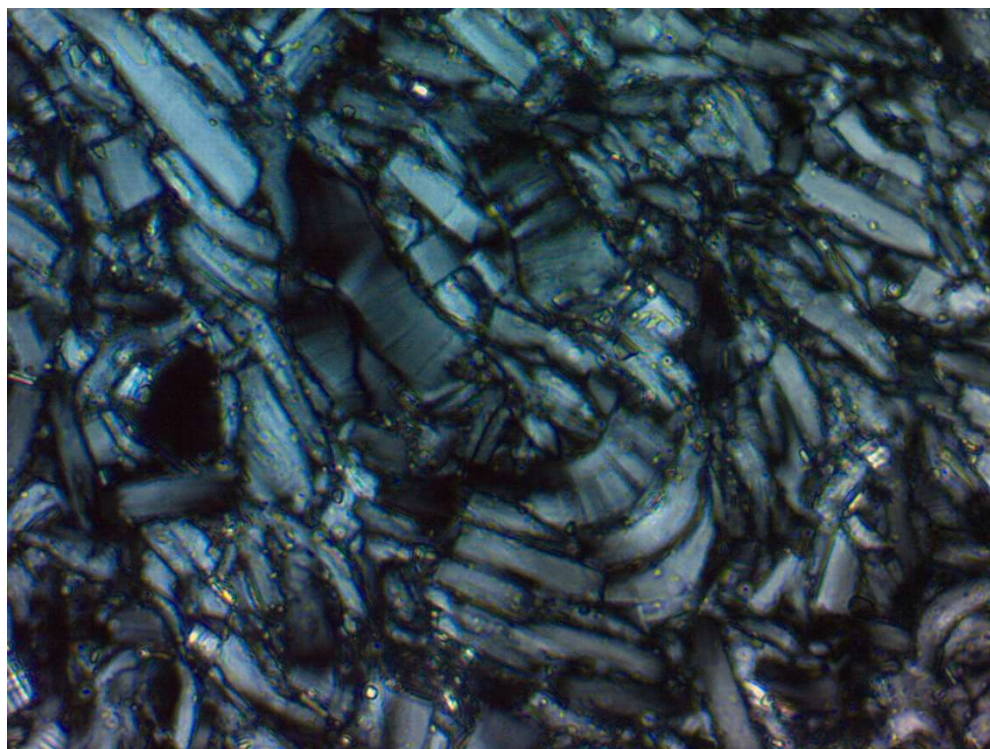


Camarel, Gabriel, Batail *Adv. Funct. Mater.* 2003,13(5) 377
 Extraction La/Ac: Thèse Camille Guiot, Dir: P. Batail ICSM, 2009

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Application from Fast & Large swelling?



To large distances
($d > 200$ nm)

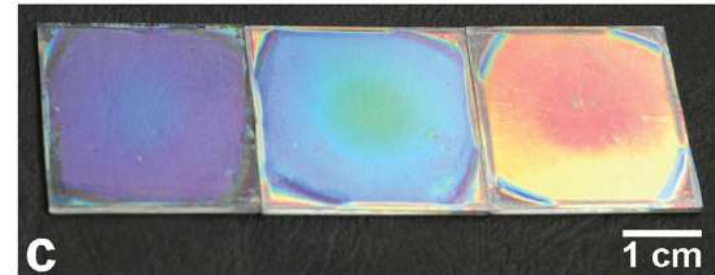
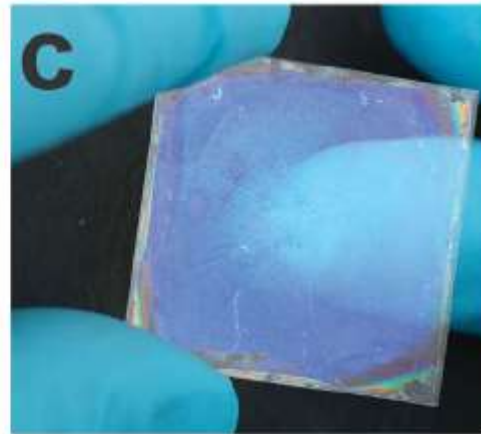
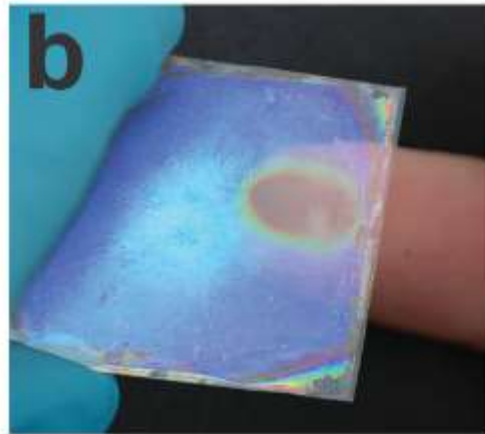
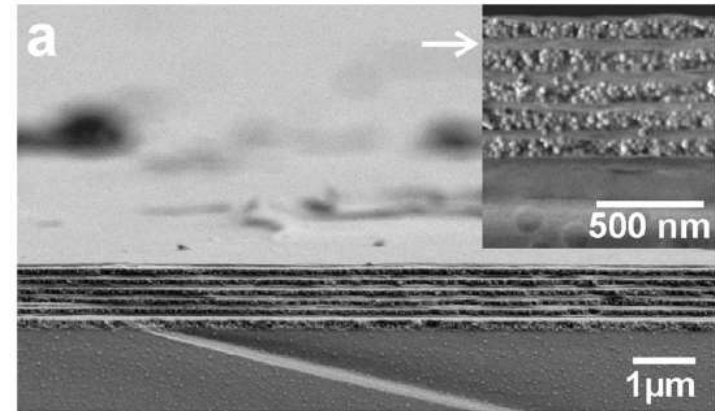
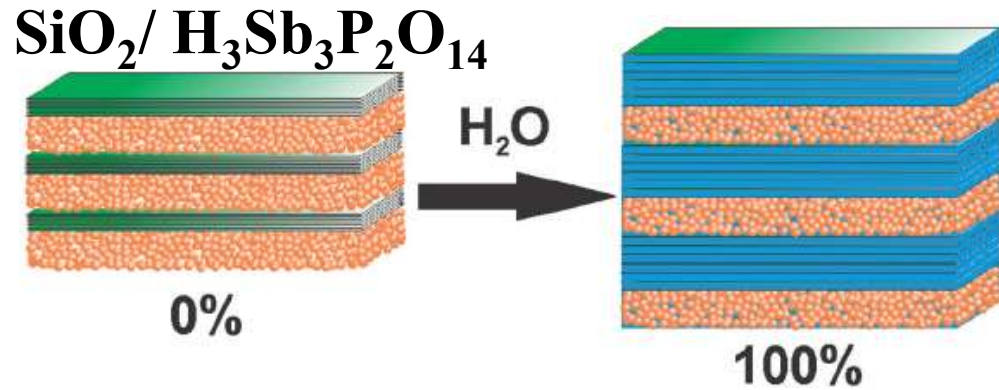
Visible light diffraction effects

al. et Batail Nature 2001

Song, Sasaki et al. *Chem. Comm.* 2015

Sano, Sasaki et al. *Nature Comm.* 2016

$\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$'s swelling integrated?



Materials Views
www.MaterialsViews.com

ADVANCED MATERIALS
www.advmat.de

Touchless Optical Finger Motion Tracking Based on 2D Nanosheets with Giant Moisture Responsiveness

Katalin Szendrei, Pirmin Ganter, Olalla Sánchez-Sobrado, Roland Eger, Alexander Kuhn, and Bettina V. Lotsch*

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Carbon nanotube based nematic phase?

Top Curr Chem (2003) 226: 119–172
DOI 10.1007/b10827

Mineral Liquid Crystals from Self-Assembly of Anisotropic Nanosystems

Jean-Christophe P. Gabriel¹, Patrick Davidson²

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E-mail: jcgabriel@nano.com

² Laboratoire de Physique des Solides, Bât. 510, UMR 8502 CNRS, Université d'Orsay, 91405 Orsay, France, *E-mail: davidson@lps.u-psud.fr*

In the recent past, and following the discovery of nanotubes by Iijima [89], there has been an enormous increase in the number of groups and reports concerning the synthesis of nanorods, nanowires, as well as nanotubes. Most of the elements of the periodic table have now been used (N.B. the difference between nanorods and nanowires is that nanorods usually have a small aspect ratio when nanowires have a high one). These particles, which present a wide range of properties such as semiconducting or metallic behavior, could lead to numerous new liquid crystalline phases and by clever exploitation of their self-assembly properties, numerous new materials with a variety of applications could be synthesized. Since the number of such phases is increasing so rapidly, we have summarized the most studied systems and what we consider to be the most original in Table 1, although we must add that this is not an exhaustive list.

Table: Possible Lyotropic Nanomaterials

Composition	Synthesis method(s)	Type
C	Arc, Laser ablation, CVD,	NT

ts reserved
ained herein
nsent of CEA

Carbon nanotube based nematic phase?

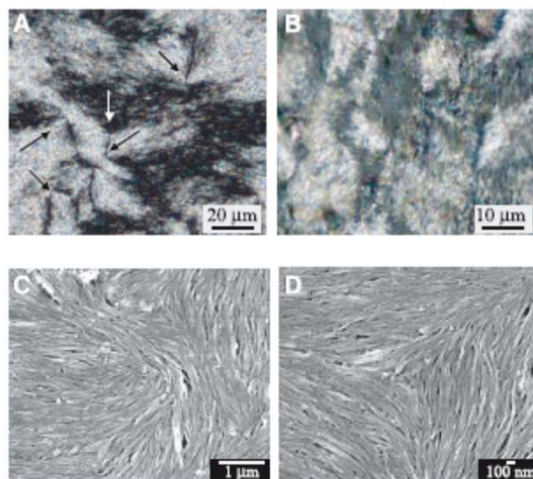
BREVIA

Nematic Liquid Crystallinity of Multiwall Carbon Nanotubes

Wenhui Song, Ian A. Kinloch, Alan H. Windle*

Carbon nanotubes show promise for a wide range of applications due to a combination of their unusual structural, mechanical, and electronic properties. However, the limited ability to process nanotubes hinders the realization of their full potential. To remove this obstacle, research has been focused on the dispersion of nanotubes in solvents through oxidation, grafting, wrapping, and surfactant addition (1). Nevertheless, their production as uniform and ordered assemblies remains a challenge. It has already been proposed that carbon nanotubes should form a lyotropic liquid crystalline phase (2), whereas lyotropic phases have been reported in other nanoscale rigid rod systems, such as the tobacco mosaic virus (TMV) (3). The formation of such a phase in carbon nanotubes should facilitate large-scale alignment during processing, as well as provide opportunities to understand further details of liquid crystalline behavior.

Carbon nanotubes show promise for a wide range of applications due to a combination of their unusual structural, mechanical, and electronic properties. However, the limited ability to process nanotubes hinders the realization of their full potential. To remove this obstacle, research has been focused on the dispersion of nanotubes in solvents through oxidation, grafting, wrapping, and surfactant addition (1). Nevertheless, their production as uniform and ordered assemblies remains a challenge. It has already been proposed that carbon nanotubes should form a lyotropic liquid crystalline phase (2), whereas lyotropic phases have been reported in other nanoscale rigid rod systems, such as the tobacco mosaic virus (TMV) (3). The formation of such a phase in carbon nanotubes should facilitate large-scale alignment during processing, as well as provide opportunities to understand further details of liquid crystalline behavior.



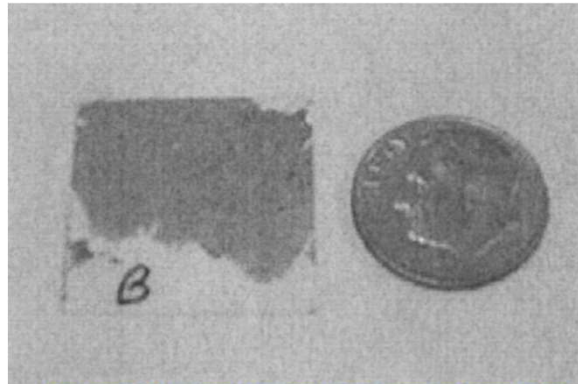
structure using the scanning electron microscope (SEM) at a resolution sufficient to view individual nanotubes (fig. S1B). In particular, it is possible to see how individual nanotubes contribute to distortions of the director field and how they are arranged in the central core of the disclinations, an issue of considerable interest in the liquid crystal field.

Figure 1, C and D, are SEM images of disclinations with a strength $+1/2$ and $-1/2$. The $+1/2$ disclination (Fig. 1C) shows that the severe bend distortion close to its core is accommodated by twist distortion between successive layers lying at slightly different depths below the surface, rather than by the bending of the rigid nanotubes themselves. The $-1/2$ disclination of Fig. 1D appears to have some shorter tubes segregated at the core. The core areas also showed evidence of holes in the parallel packing of the nanotubes, which, while reminding one of the considerable shrinkage of the material resulting from the drying process, may also suggest a lower concentration of nanotubes in regions of high distortion, especially splay. SEM examination of the fracture surfaces of thick samples dried in a rubber mold showed that a multidomain structure was also present throughout the sample and that the surfaces were quite typical.

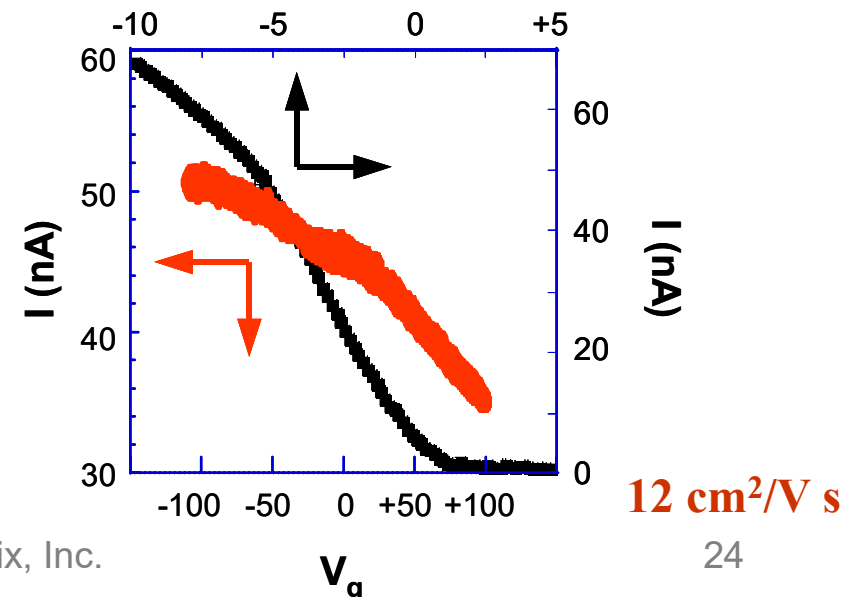
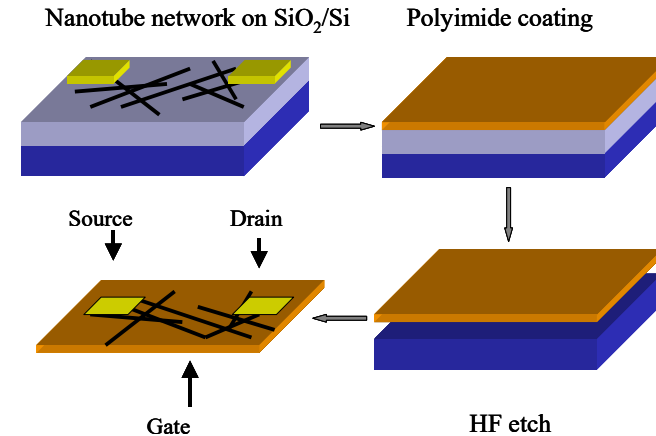
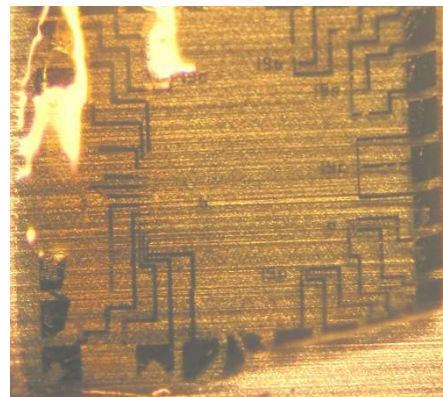
Nanotubes have been shown to form a liquid crystalline phase, as predicted by rigid rod theory (9, 10). The phase should provide further

Experimental observation: W. Song, I. A. Kinloch, A. H. Windle *Science* **302**, 1363 (2003)

Flexible Electronics?



⇒ SC /Conducting / Transparent flexible films/FET (Displays) – Startup Unidym CVD Growth/Sprayed/LB Sold to Arrowhead Research Corp.



© Nanomix, Inc.

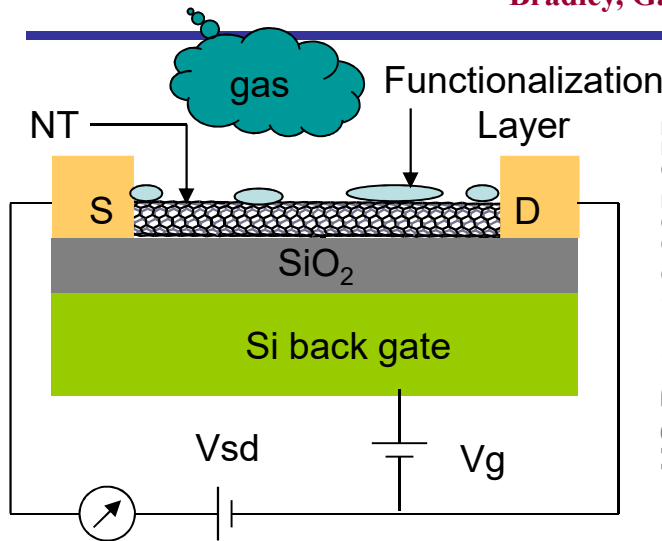
FET: a Platform for Gas sensing



« Gas Sensor Array Based on Metal-Decorated Carbon Nanotubes. » *J. Phys. Chem. B.* 110(42); 21014-21020, 2006

Star, Gabriel and co workers « Nanoelectronic Carbon Dioxide Sensors. » *Adv. Mater.*, 16(22) 2049-2052, 2004 (Cover).

Bradley, Gabriel and co workers PRL 91(21) 218301 (2003)



US Patent 6,905,655

FL = Ni/Pd



Launch in May 2005

FL = PE + Enzyme



US Patent 7,714,398

No Go 3m prior to launch

Gases Reactivity Challenge

- Ar
- CH₄
- Hydrocarbons
- N₂, CO₂
- H₂
- CO, NO, NO₂, NH₃
- SO₂, SO₃
- O₂, O₃



Copyright, Nanomix, Inc.

FL = Al₂O₃

US Patent 8,152,991



Mai 2007: \$10 M

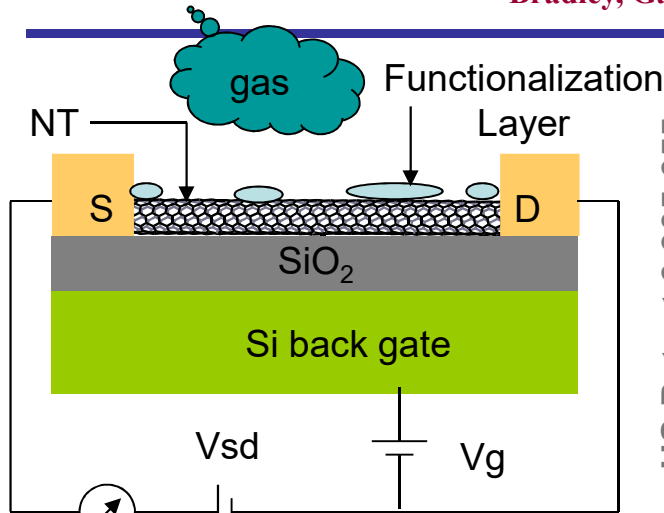
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US Patent 6,905,655

FL = Ni/Pd



Launch in May 2005

FL = PE + Enzyme



US Patent 7,714,398

No Go 3m prior

The Motley Fool

Latest Stock Picks

Investing Basics

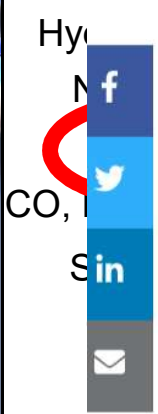
Stock Market

Retirement

Personal Fin

Nanomix With a Nano First

A commercial launch brings nanotechnology one step closer to the mainstream.



Carl Wherrett (XMFBreakerCarl)

Updated: Nov 16, 2016 at 2:09PM

Published: May 16, 2005 at 12:00AM

It is widely believed that the commercialization of nanotechnology will come courtesy of "big boys" like **IBM** (NYSE:IBM), **Intel** (NASDAQ:INTC), or another 800-pound gorilla. But last week, private California-based **Nanomix** announced its first commercial product launch: a hydrogen gas-detection device for use in industrial settings, based on the company's patented "Sensation" detection technology.

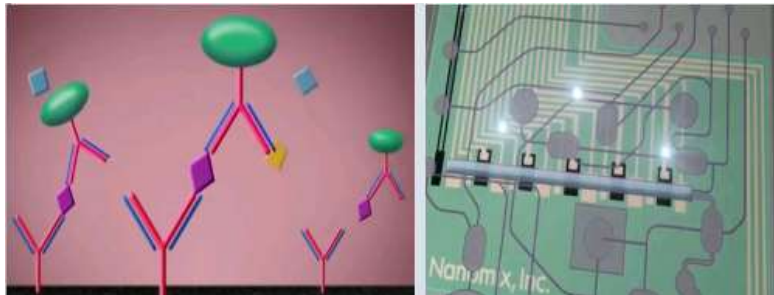
CNT sensors: EBOLA Crisis

FL = PEG + AntiBody:

=> **Electronic detection of specific Antigen's binding using nanotube FET devices**

A Star, JCP Gabriel, K Bradley, G Grüner. *Nano letters* 3 (4), 459-463 (960 citations)

=> US Patent 6,894,359 (220 cit.) etc.



2014

The Nanomix System

The fully automated Nanomix system consists of a handheld reader and integrated, self-contained assay cartridge with a carbon nanostructure biosensor.



- * Laboratory Quality Testing at the Point of Patient Care
- * Delivered Rapidly and Cost Effectively
- * Portable, Electronic Detection and Data Availability
- * Multiple tests from a single patient sample

2021: COVID-19
02/21: FDA Fast-track
 => on Sale 2021

=> ~~nano.com~~ => **nanomixdx.com**

■ Bubble Deposition Method (BDM)

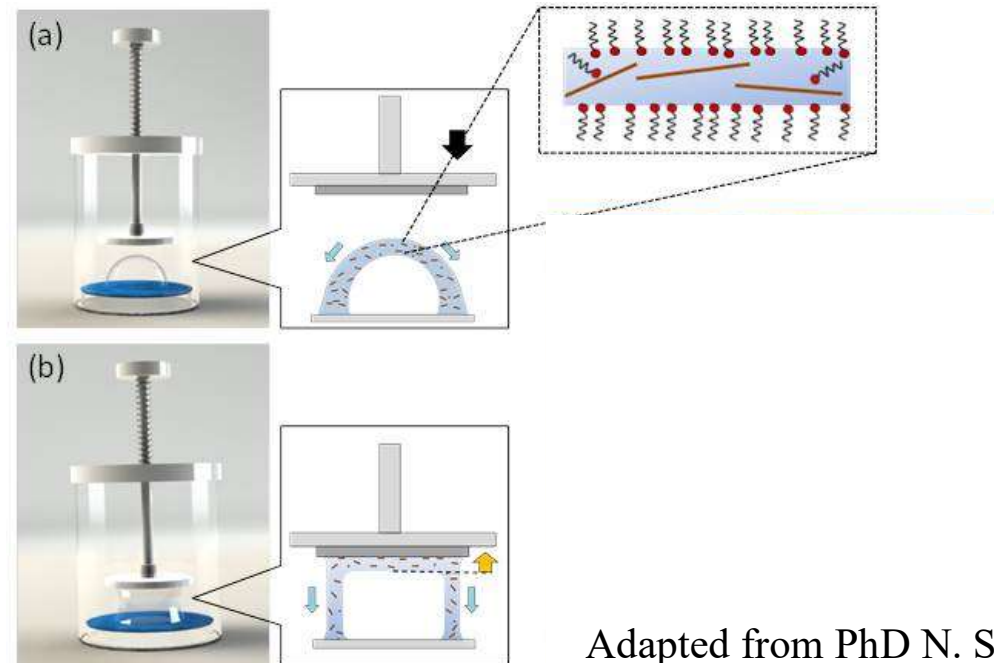
- Method initially developed and optimised @ CEA [J. Azevedo, J.J. Benattar, V. Derycke]

■ Principle

- Transfer of thin water film containing nanostructures and stabilized by surfactants: « soap bubble »

■ After transfert

- Single layer
- Low roughness (1 nm)
- Thin (1.5 nm)

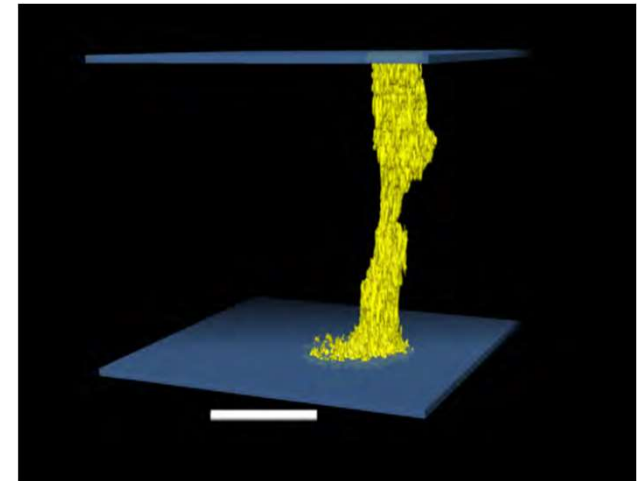


JJ Benattar *Angew. Chem.* 45(25) 2006, 4186
Azevedo et al. *App. Mater & Interfaces* 2016

Adapted from PhD N. Sridi

Conclusions & Perspectives: A Tribute to Patrick's

- 1D & 2D Solids have lots of potentiel
- We've only scratched the surface
- Many experimental results unexplained by modelisation or even theory; many challenges:
 - Charged anisotropic colloids models
 - Transition metals
 - Hydrogen bonds
 - Solubilization theory
- **Hybrids Organic/inorganic**



P. Davidson, C. Safinya and coworkers *Scientific Reports 2018*: Clays + DNA

Galland et al. *Nat. Mater.* & Gabriel et al. Patent app. n°EP2626367A1 « Method for obtaining 3D actin structures and uses thereof ».

K. El Rifaii, H. H. Wensink, T. Bizien, JCP. Gabriel, L. Michot, P. Davidson « Destabilization of the Nematic Phase of Clay Nanosheet Suspensions by Polymer Adsorption », *Langmuir* 36(42) 12563–12571 (2020)

Conclusions & Perspectives – Applications

- They are now in consumer electronic products
 - Integrating them into products can be costly
 - The IP landscape is very busy
 - Development cost write off is difficult => large markets
 - Future research
 - Water quality sensors and other devices (3 funded projects, 2D-MEMBA)
 - Thin films applications
 - E-waste recycling: Joint Lab CEA-Singapour SCARCE (2018-2022)
- => Now hiring (engineers and postdocs etc...)**

Alain Penicaud

Acknowledgement: **P. Batail et al.**

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- C. Bourgaux
- **K. Bradley**
- A.M. Bravo
- R. Brec
- M. Briman
- **F. Camerel**
- **A.K. Cheetham**
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- F. Ezzahra
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- **S. Skapuro**
- C. Sourisseau
- M. Spano
- **J.P. Sprunck**
- G. Srdanov
- **N. Sridi**
- **A. Star**
- **C. Sun**
- D. Thomas
- E. Tu
- S. Uriel
- **C. Valcke**
- **S.J. Weigel**
- **F. Wudl**
- P. Zhou
- **T. Zemb**

And many more + ITAs



Grant n° 320915
2013-2018



ANR-17-CE04-0003
2017-2022



USS-IF-2018-4
2018-2022



Arrival IMN, Nantes 01/01/1997

Ice blocks in la Loire



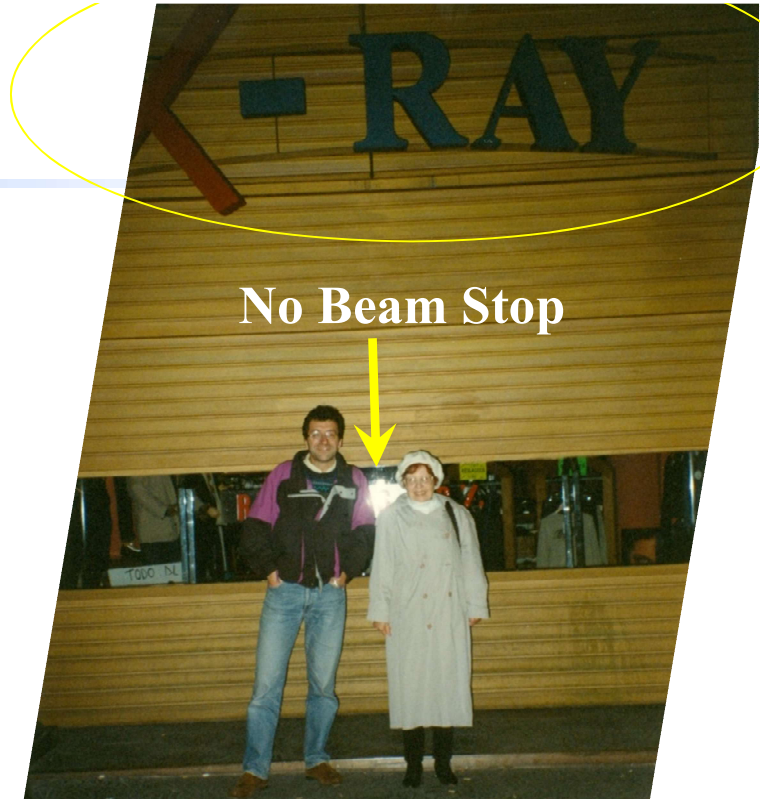
Dr. Lucy M. Bull (1968 – 2006)

=> Solid State NMR in Nantes



**Kim
Dunbar
Rimma
Shibaeva**

01/1998 Sitges, Barcelona



No Beam Stop



Patrick's group: Match Making

**Rodolphe
Clérac**



05/1998 Noirmoutier, CONCOORD'98

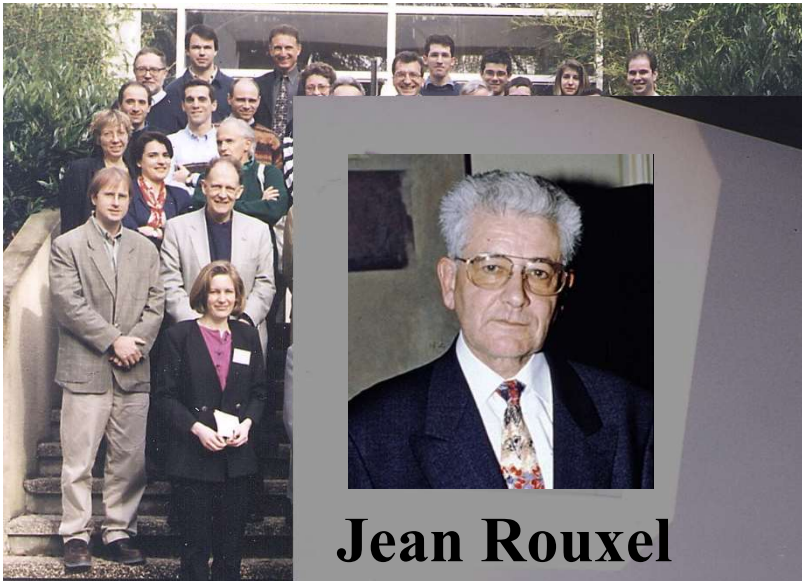


05/1998 Noirmoutier, CONCOORD'98

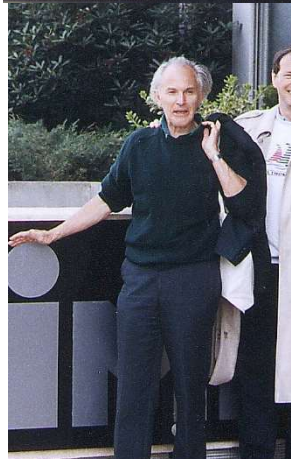


1999 MRL-IMN Workshop, IMN Nantes





Jean Rouxel
1935-1998



1999 MRL-IMN Workshop, IMN Nantes



After the drawing, the sculpture!



THANK YOU PATRICK!!!

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