Can Non-Photochemical Laser induced Nucleation be a stereoselective Process?

Melody Briard, Clément Brandel, Valérie Dupray, Gérard Coquerel

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Context

NPLIN stands for Non-Photochemical Laser Induced Nucleation.

- Nucleation process discovered in 1996 by Garetz *et al* (1)
- *Laser pulses triggers nucleation from supersaturated solution*
- *How does it works ?* ➔ *Different Hypotheses*

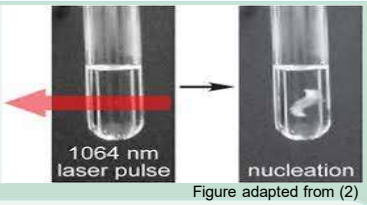
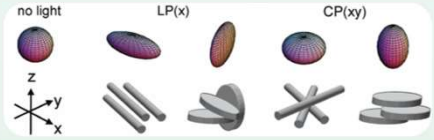


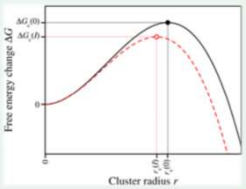
Figure adapted from (2)

OKE : Optical Kerr Effect

Alignment of the dipole along the electromagnetic field

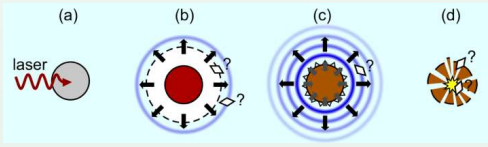


DP : Dielectric Polarization



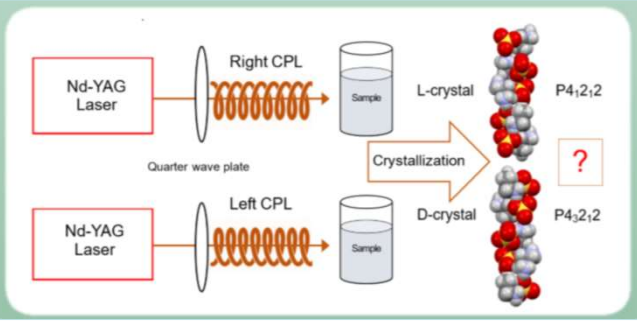
Decrease of the free energy of nucleation due to the electromagnetic field

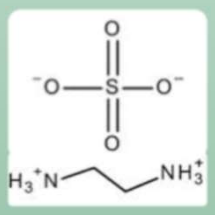
Cavitation : bubble generation



Figures adapted from (3)

Can **chirality** be used to identify the **NPLIN mechanism**?



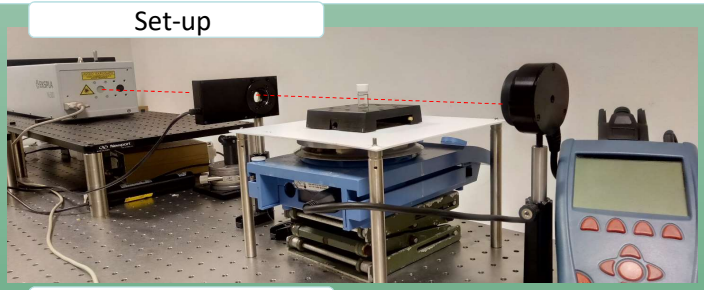


Ethylenediamine sulfate (EDS)

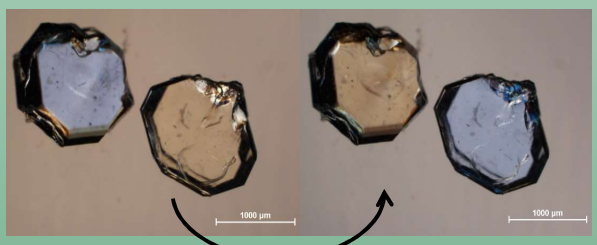
- Supramolecular chirality $P4_12_12$ or $P4_32_12$
- Easy to distinguish enantiomorphs
- The nucleation can be triggered by laser pulses

Results & Discussion

Set-up



Crystals obtained



Anticlockwise rotation of the polarizer of the optical microscope

Results :

Polarization	N_{vial}	$N_{crystal}$	N_D	N_L	Cee±σ
Left Circularly Polarized Light	89	194	99	95	0.02±0.07
Right Circularly Polarized Light	86	190	81	109	-0.14±0.07
Linearly Polarized Light	91	251	129	122	0.03±0.06

Supersaturated solution (β=1.1), exposed to 1 laser pulse at 34.8mJ (1064 nm)
The Crystal Enantiomeric Excess (**Cee**) shows no significant change upon changing laser polarization geometry
It is in our experience that the NPLIN process of $NaClO_3$ from aqueous solutions is also not stereoselective (data not shown here)

Why is there no influence of polarized light ?

Option n° 1

OKE mechanism is invalid

The electromagnetic field of the laser can not influence the orientation of the molecules

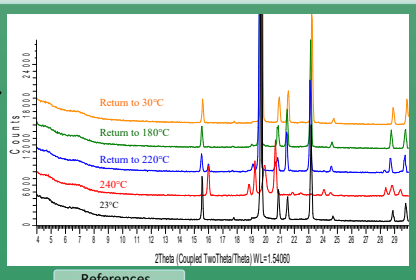
Option n° 2

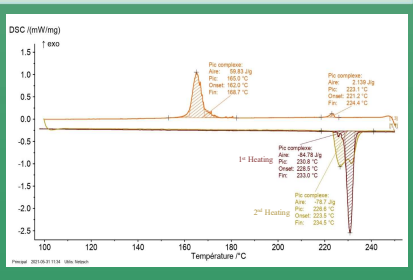
Potential Metastable phase

Supersaturated solution → Laser → Metastable phase → Spontaneous crystallization → Chiral phase L or D crystals

As in the case of $NaClO_3$(3),an achiral phase nucleates first and transforms non stereoselectively into the chiral one (monotropic system). So the laser can not induce any stereoselective effect.

Existence of a High-Temperature phase of EDS, likely centrosymmetric
Does laser trigger its nucleation first?
It is unlikely : due to the high transition temperature (ca. 230°C)
(Enantiotropic system)





Conclusion & perspectives

NPLIN seems to be non-stereoselective
BUT experiments with chiral molecules are needed to confirm it EVEN IF OKE is already controversial (4),(5) (invalid option 1)
Another option would be another mechanism : we think that Cavitation mechanism is more likely and we will focus our next studies on it

References
(1) Garetz, B. A.; Aber, J. E.; Goddard, N. L.; Young, R. G.; Myerson, A. S. *Physical review letters* 1996, *77* (16), 3475.
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(3) Alexander, A. J.; Camp, P. J. Non-Photochemical Laser-Induced Nucleation. *J. Chem. Phys.* **2019**, *150* (4), 040901.
(4) Barber, E. R.; Kinney, N. L. H.; Alexander, A. J. *Crystal Growth & Design* 2019, acs.cgd.9b00951.
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