Chimie de surface et procédés thermo-électriques pour de nouvelles fonctionnalités à la surface de matériaux vitreux

MARC DUSSAUZE, LUC VELLUTINI, FREDERIC ADAMIETZ, VINCENT RODRIGUEZ, LIONEL CANIONI, SYLVAIN DANTO, YANNICK PETIT, VERONIQUE JUBERA, THIERRY CARDINAL

INSTITUT DES SCIENCES MOLÉCULAIRES, UMR 5255, UNIVERSITÉ DE BORDEAUX, 351 COURS DE LA LIBÉRATION, TALENCE CEDEX 33405, FRANCE

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USTV / Dijon 2024

LIGHTTech

Mise en forme, fonctionnalisation et
Impression Laser 3D de composants photoniques.

Marc Dussauze, Frederic Adamietz, David Talaga, Vincent Rodriguez

Plateforme SIV (Spectroscopie et imagerie Vibrationnelle)
Raman, IR (20 spectromètres, 15 permanents)
Analyse structurale, Analyse de surface
Optique non linéaire

Poling thermique

Luc Vellutini

Chimie de surface
Bio fonctionnalisation

Chimie du verre Thierry Cardinal, Sylvain Danto, Veronique Jubera

Verres Phosphate d'argent photosensible
Verres pour l'optique non linéaire
Verres d'oxyde lourd pour l'IR
Verres chalcogénures
Matériaux Luminescents

Fibrage
Couche mince

Irradiation laser femto seconde Yannick Petit, Lionel Canioni

SURFACE BIO-FUNCTIONALIZATION OF CHALCOGENIDE GLASS FIBER TO ENHANCE REAL-TIME AND LABEL-FREE MID-INFRARED BIO DETECTION

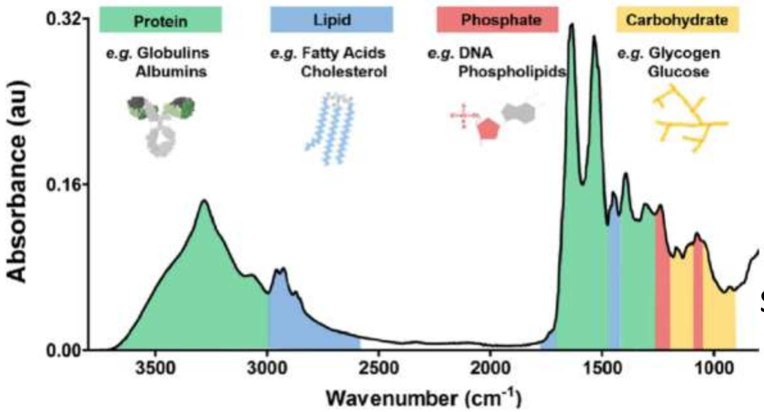
RAYAN ZAITER, RICARDO ALVARADO, FRÉDÉRIC ADAMIETZ, FRÉDÉRIC DÉSÉVÉDAVY, CLÉMENT STRUTYNSKI, DAMIEN BAILLEUL, FRÉDÉRIC SMEKTALA, THIERRY BUFFETEAU, LUC VELLUTINI, **MARC DUSSAUZE**

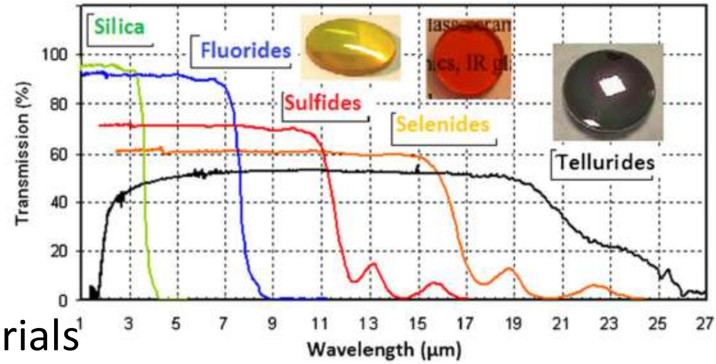
INSTITUT DES SCIENCES MOLÉCULAIRES, UMR 5255, UNIVERSITÉ DE BORDEAUX, 351 COURS DE LA LIBÉRATION, TALENCE CEDEX 33405, FRANCE

LABORATOIRE INTERDISCIPLINAIRE CARNOT DE BOURGOGNE, UMR 6303 CNRS-UNIVERSITÉ DE BOURGOGNE , 9 AVENUE ALAIN SAVARY, 21078 DIJON, FRANCE

Fiber Based IR sepctroscopy for bio-detection

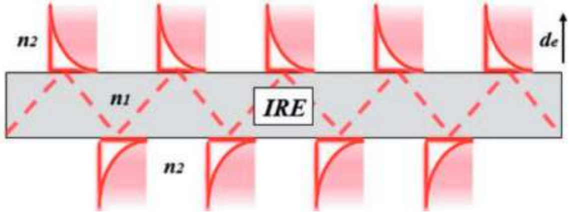
Blood serum signature up to mid-IR

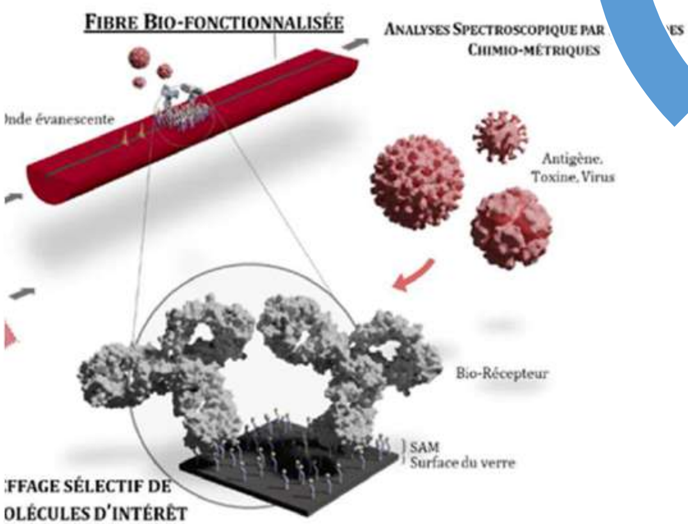




IR spectroscopy

IR optical materials
Optical fiber



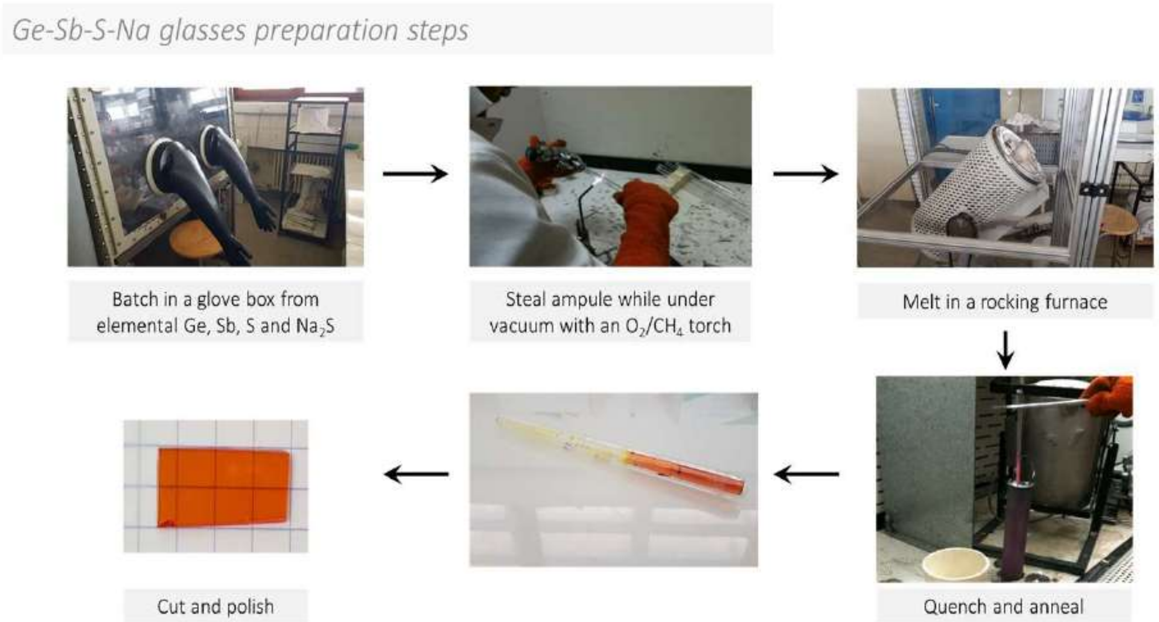


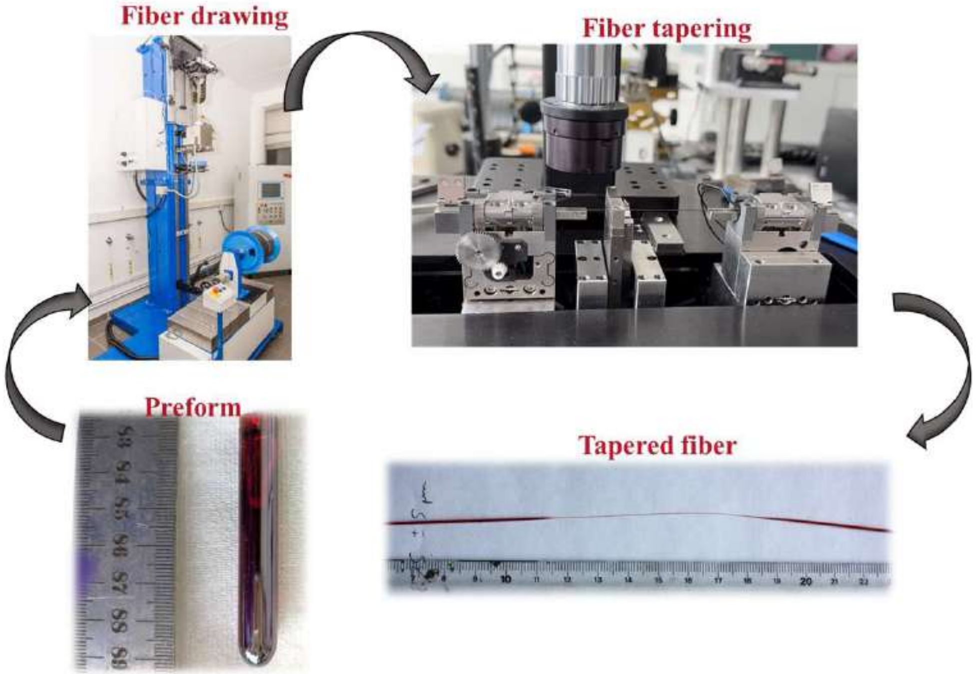
Biofunctionalization

Biofunctionality :

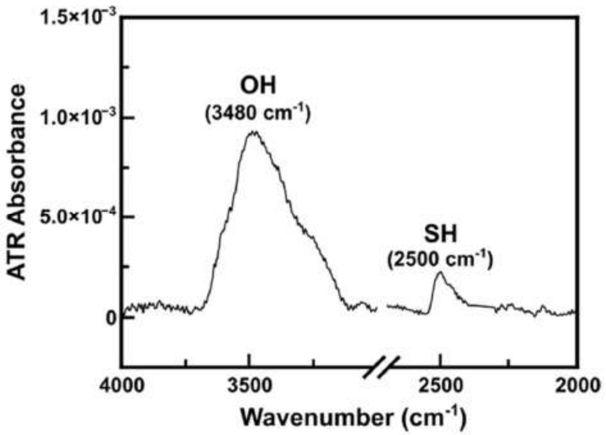
- ✓ Increase IR sensitivity
- ✓ Add selectivity

$Ge_{25}Sb_{10}S_{65}$

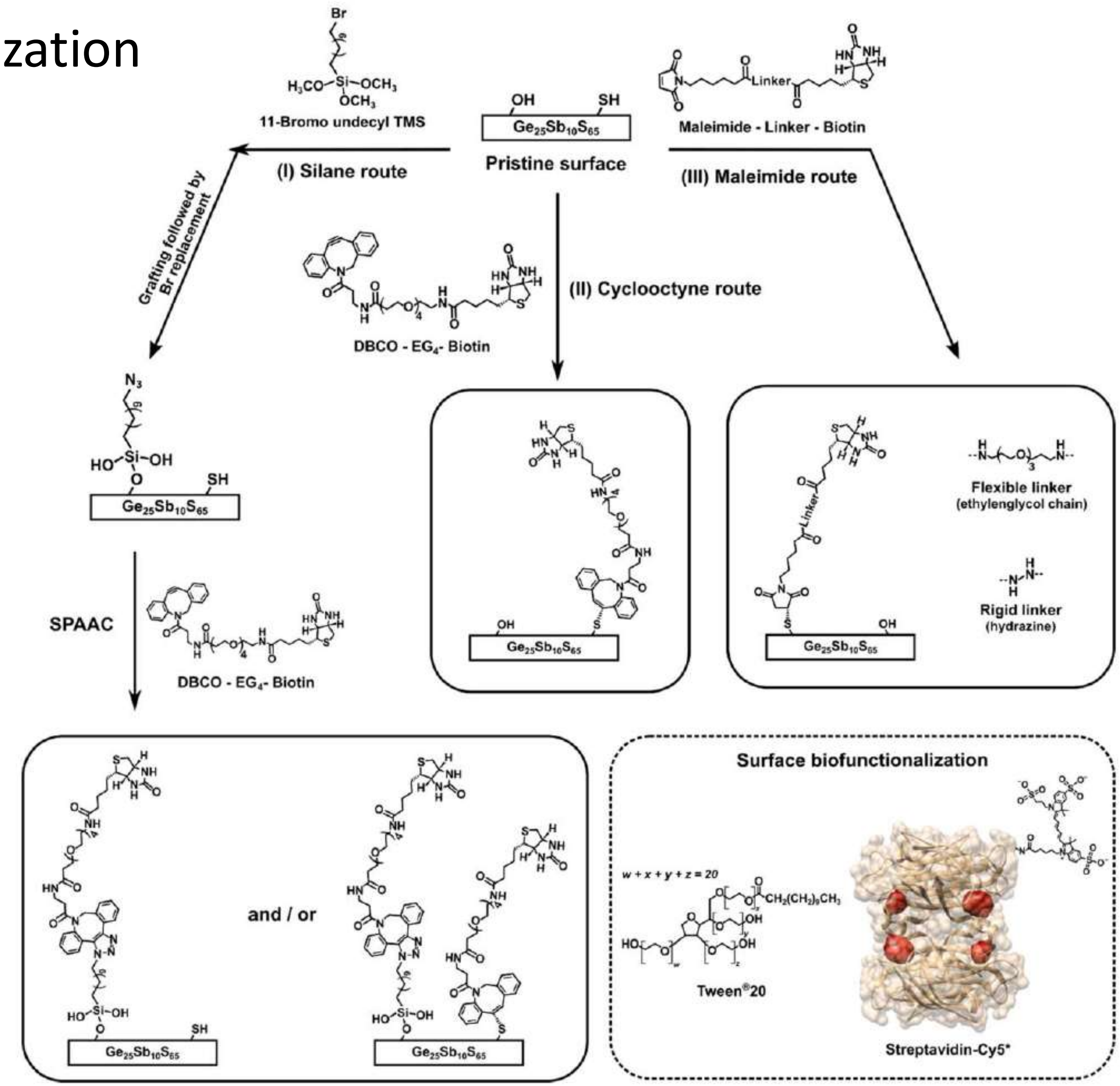




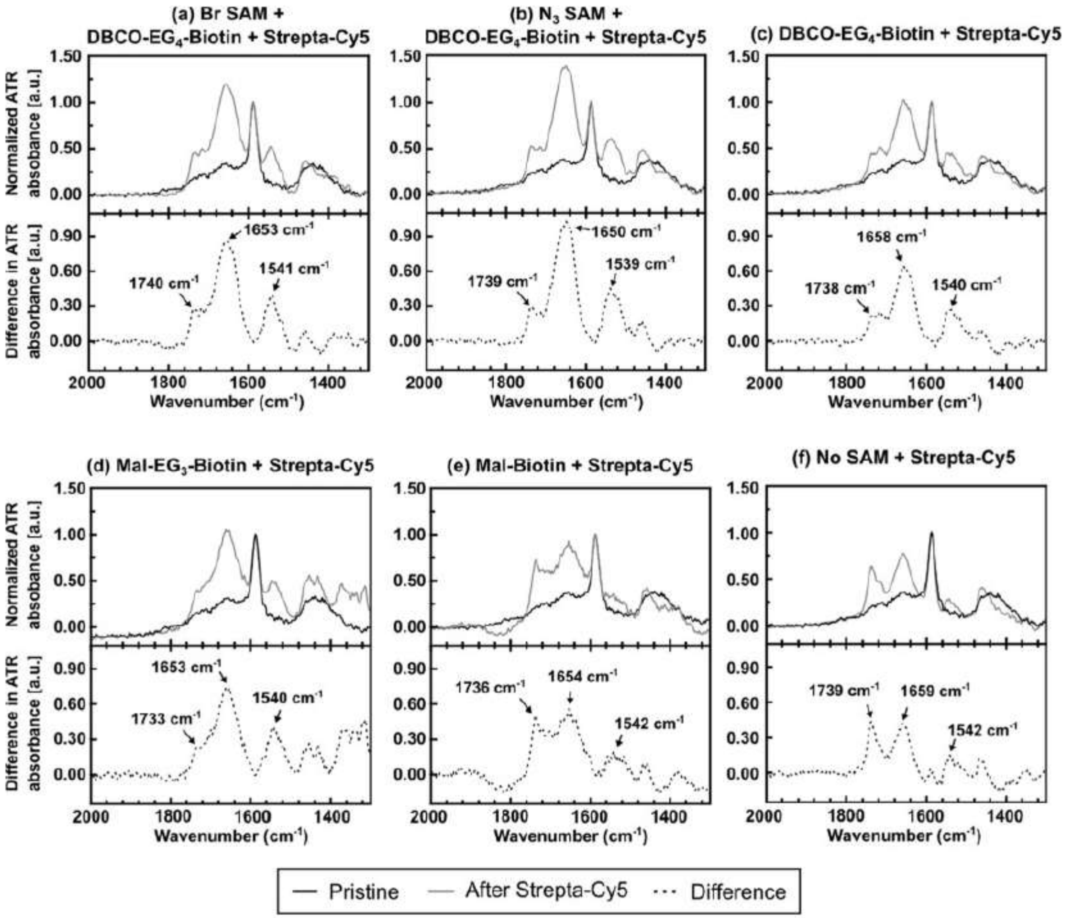
Methods for surface biofunctionalization

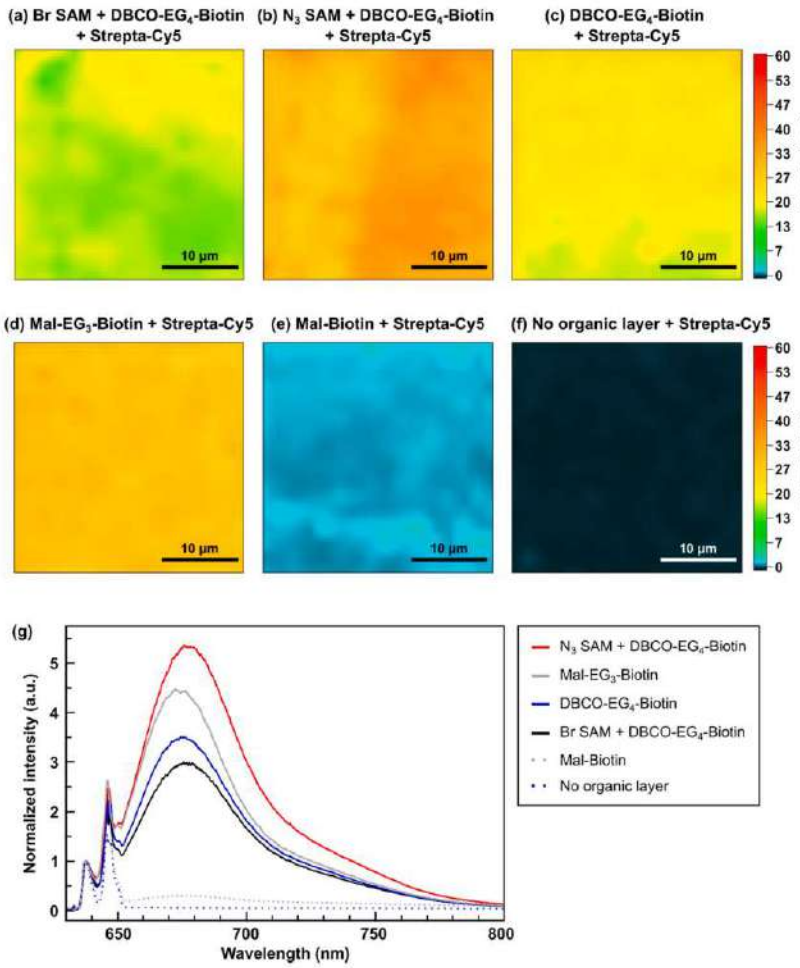


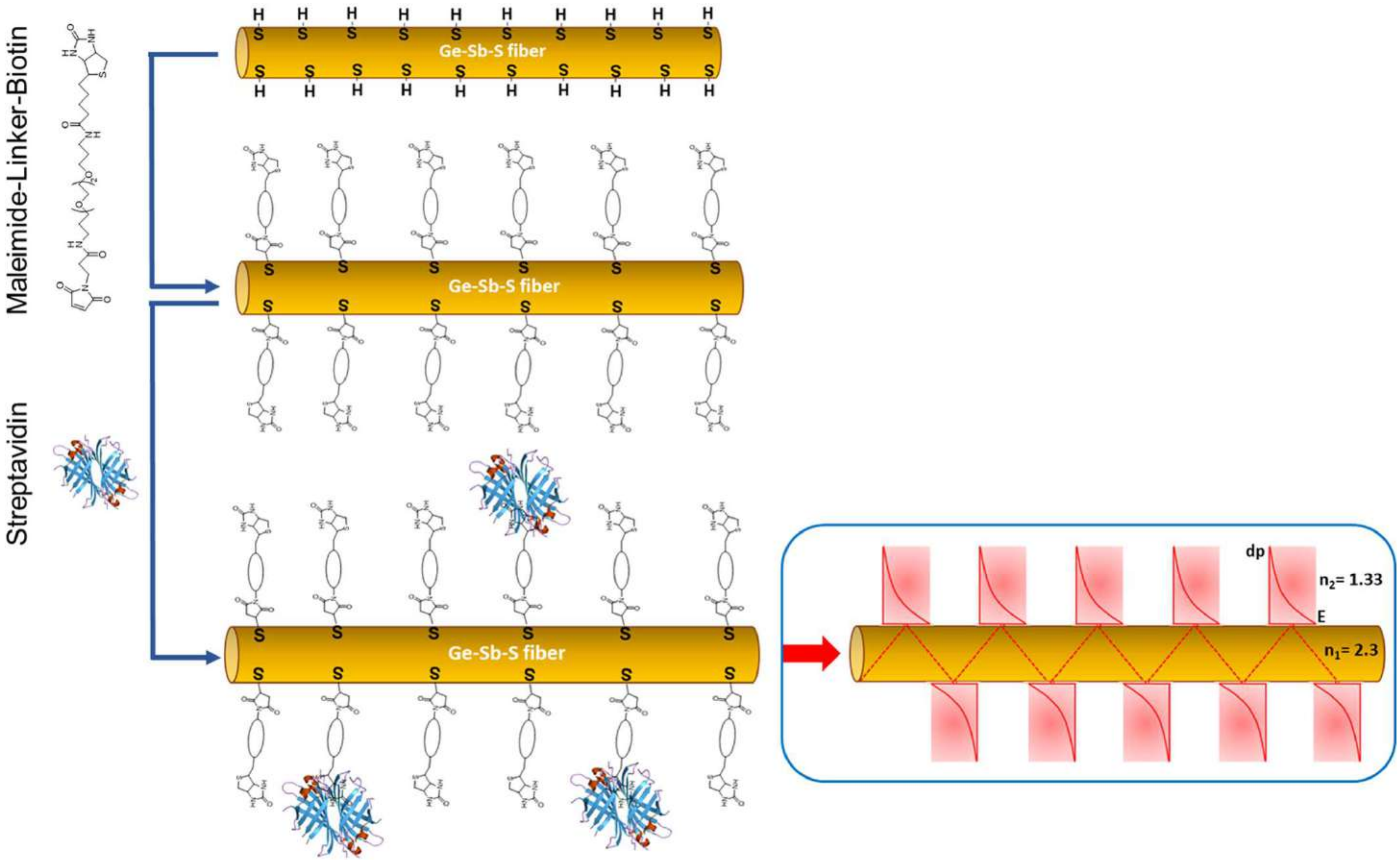
ATR IR spectra of pristine GeSbS glass

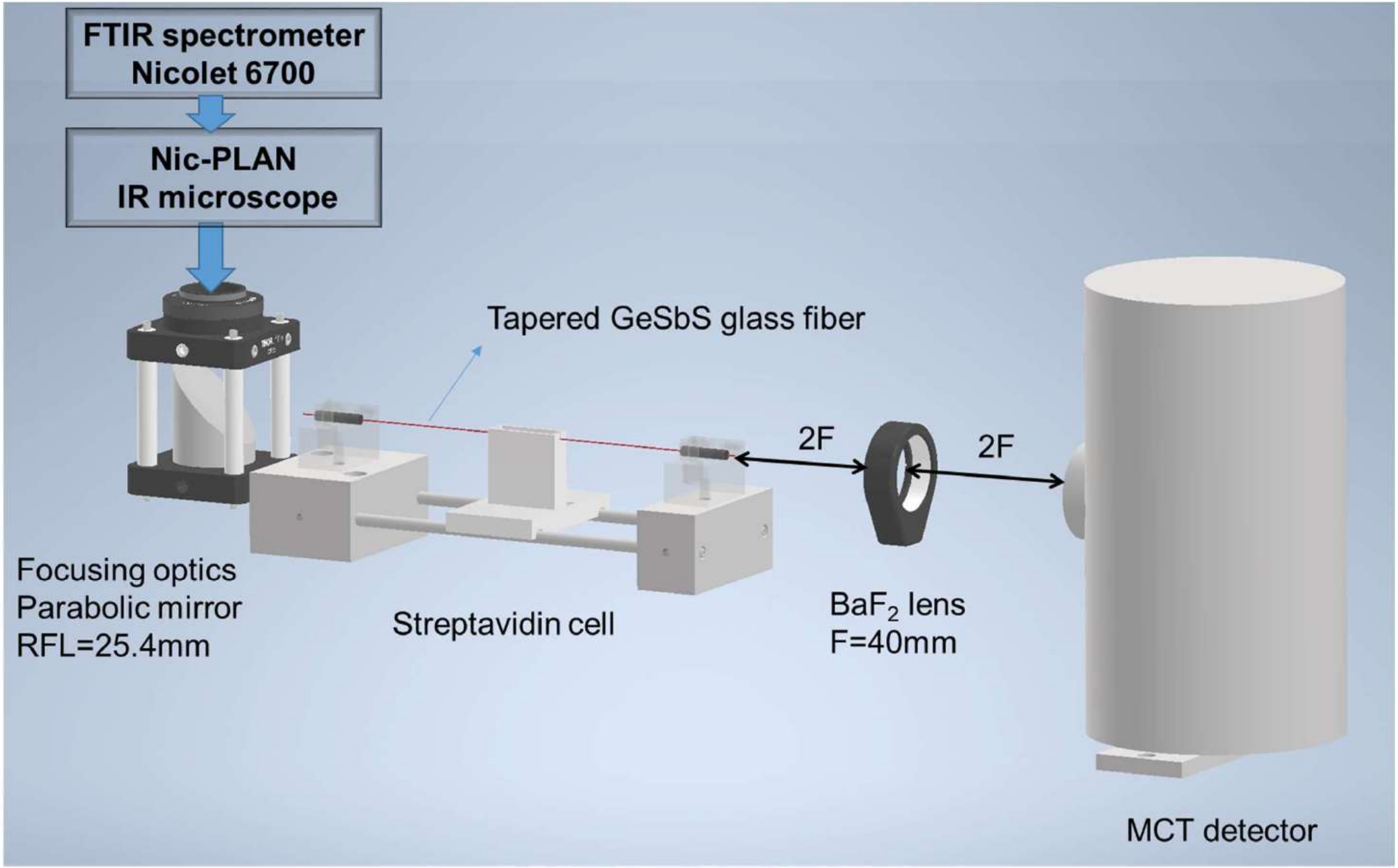


Applied Surface Science 573 (2022) 151589

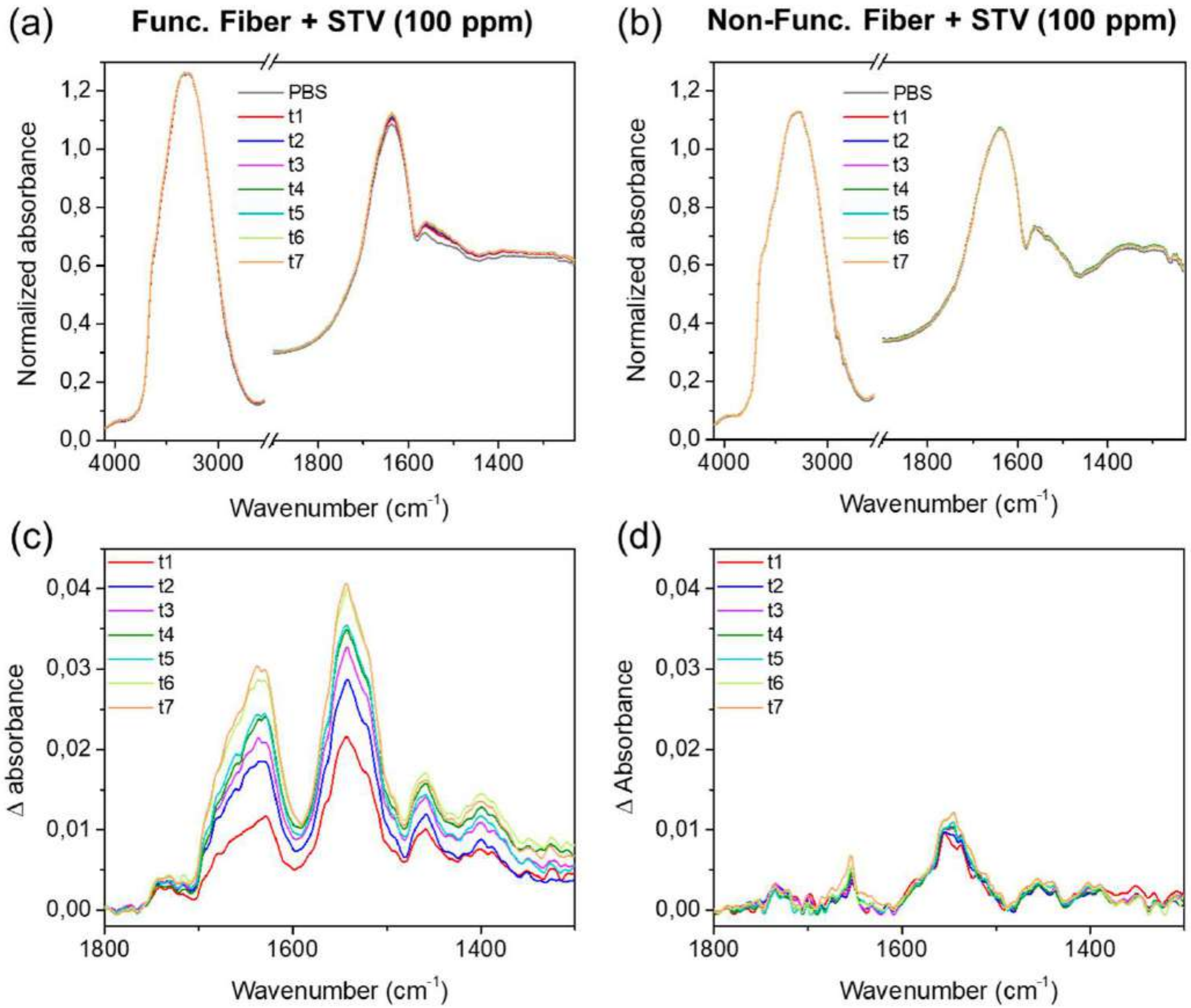

(a) Br SAM + DBCO-EG$_4$-Biotin + Strepta-Cy5
(b) N$_3$ SAM + DBCO-EG$_4$-Biotin + Strepta-Cy5
(c) DBCO-EG$_4$-Biotin + Strepta-Cy5
(d) Mal-EG$_3$-Biotin + Strepta-Cy5
(e) Mal-Biotin + Strepta-Cy5
(f) No SAM + Strepta-Cy5
Normalized ATR absorbance [a.u.]
Difference in ATR absorbance [a.u.]
Wavenumber (cm^{-1})
1740 cm^{-1}
1653 cm^{-1}
1541 cm^{-1}
1739 cm^{-1}
1650 cm^{-1}
1539 cm^{-1}
1738 cm^{-1}
1658 cm^{-1}
1540 cm^{-1}
1733 cm^{-1}
1653 cm^{-1}
1540 cm^{-1}
1736 cm^{-1}
1654 cm^{-1}
1542 cm^{-1}
1739 cm^{-1}
1659 cm^{-1}
1542 cm^{-1}
Pristine
After Strepta-Cy5
Difference


(a) Br SAM + DBCO-EG$_4$-Biotin + Strepta-Cy5
(b) N$_3$ SAM + DBCO-EG$_4$-Biotin + Strepta-Cy5
(c) DBCO-EG$_4$-Biotin + Strepta-Cy5
(d) Mal-EG$_3$-Biotin + Strepta-Cy5
(e) Mal-Biotin + Strepta-Cy5
(f) No organic layer + Strepta-Cy5
10 µm
Intensity (a.u.)
(g)
Normalized Intensity (a.u.)
Wavelength (nm)
N$_3$ SAM + DBCO-EG$_4$-Biotin
Mal-EG$_3$-Biotin
DBCO-EG$_4$-Biotin
Br SAM + DBCO-EG$_4$-Biotin
Mal-Biotin
No organic layer

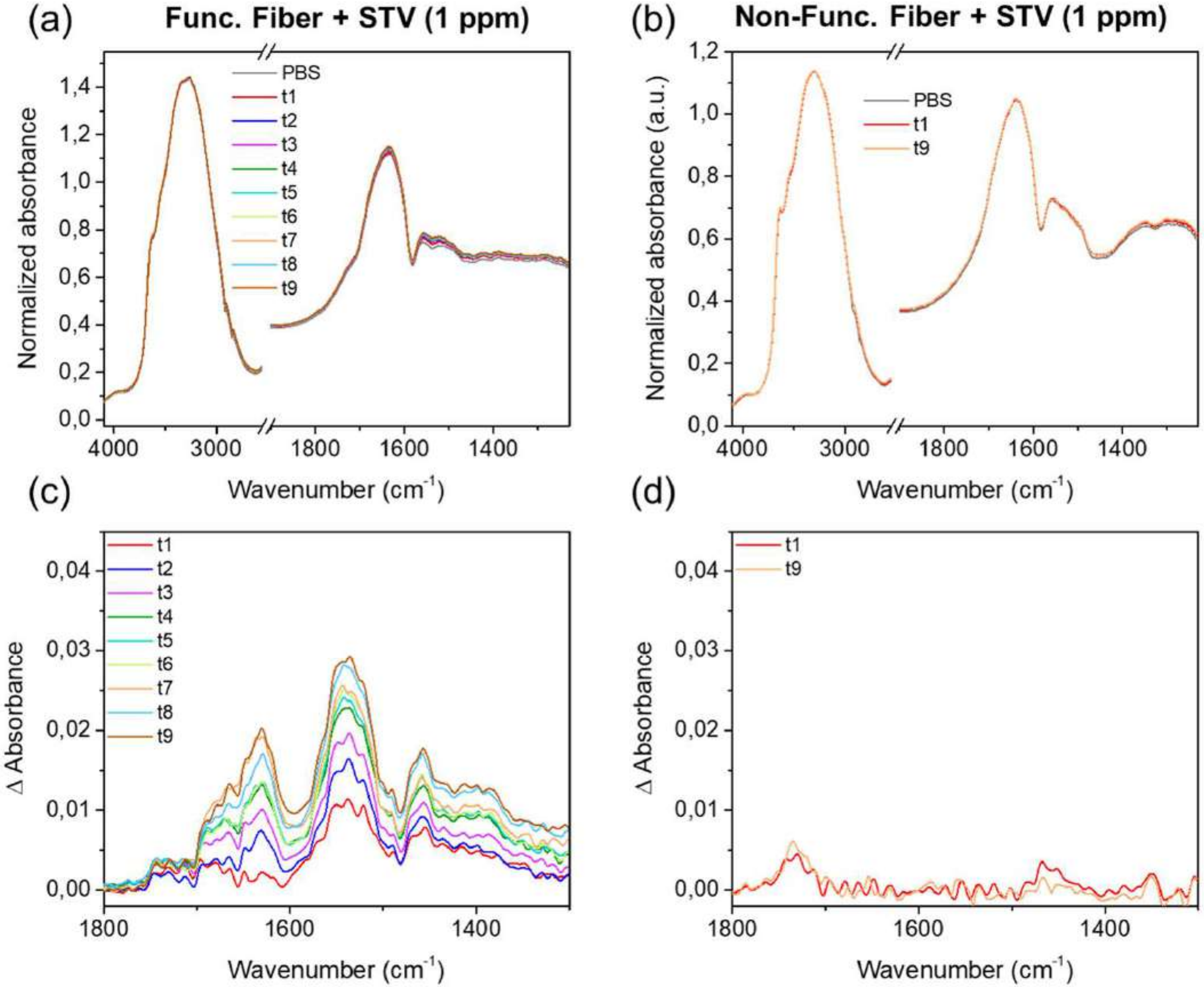

Maleimide-Linker-Biotin
Streptavidin
Ge-Sb-S fiber
Ge-Sb-S fiber
Ge-Sb-S fiber
dp
n_2= 1.33
E
n_1= 2.3


FTIR spectrometer
Nicolet 6700
Nic-PLAN
IR microscope
Tapered GeSbS glass fiber
2F
2F
Focusing optics
Parabolic mirror
RFL=25.4mm
Streptavidin cell
BaF2 lens
F=40mm
MCT detector

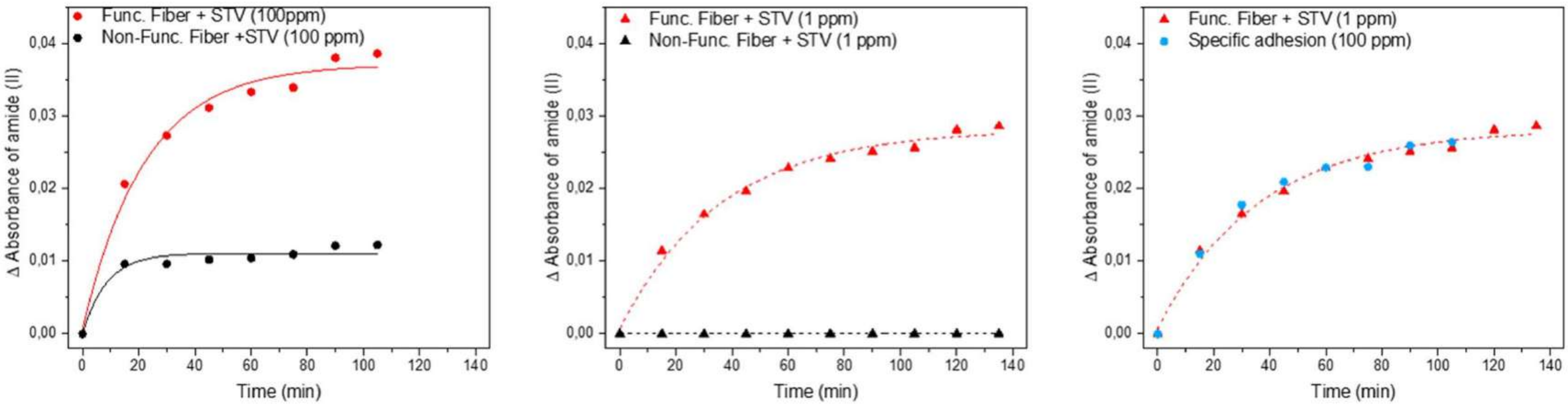
STV detection at 10O ppm



STV detection at 1 ppm

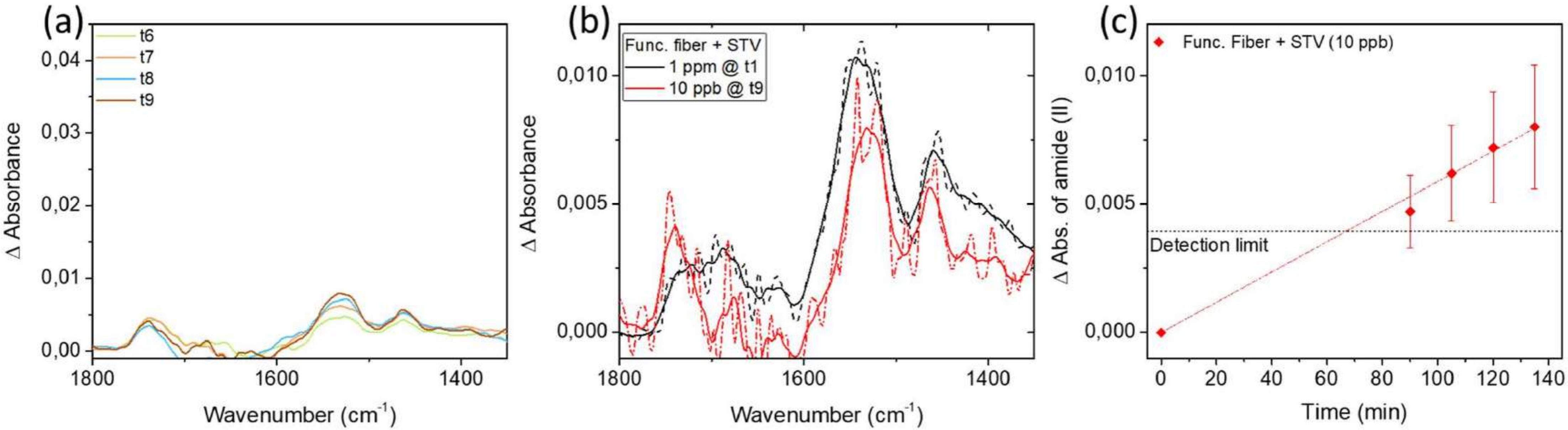


Kinetic vs. STV concentration



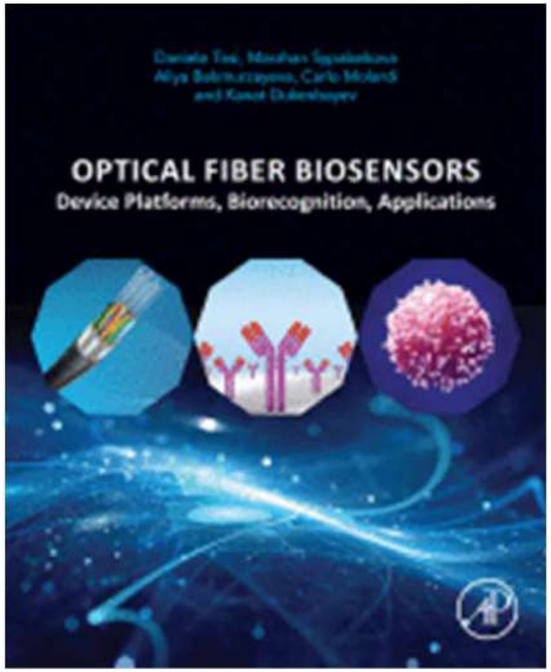
STV concentration at the probe surface governed by the surface bio-functionality and not limited by the STV volumetric concentration and diffusion processes

STV detection at 10ppb



Optical biosensor based on biofunctionalized fiber

V. Voisin, J. Pilate, P. Damman, P. Mégret, and C. Caucheteur, "Highly sensitive detection of molecular interactions with plasmonic optical fiber grating sensors," *Biosensors and Bioelectronics*, vol. 51, pp. 249–254, Jan. 2014, doi: 10.1016/j.bios.2013.07.030.



IR sensing based on tapered chalcogenide glasses.:

Hocdé *et al.* have tapered Te-As-Se fibers from a diameter of 400 µm down to 100 µm to measure the concentration of acetone diluted in mythylene chloride, they obtained values as low as 2.5%.

S. Hocdé, C. Boussard-Plédel, G. Fonteneau, D. Lecoq, H.-L. Ma, and J. Lucas, "Recent developments in chemical sensing using infrared glass fibers," *Journal of Non-Crystalline Solids*, vol. 274, no. 1, pp. 17–22, Sep. 2000, doi: 10.1016/S0022-3093(00)00179-4.

Le Coq *et al.* have employed Te-As-Se fibers tapered to a diameter of 50 µm to detect ethanol in water and a detection limit of 0.5% was acquired.

D. Le Coq, C. Boussard-Plédel, G. Fonteneau, T. Pain, B. Bureau, and J. L. Adam, "Chalcogenide double index fibers: fabrication, design, and application as a chemical sensor," *Materials Research Bulletin*, vol. 38, no. 13, pp. 1745–1754, Oct. 2003, doi: 10.1016/j.materresbull.2003.07.003.

Velmuzhov *et al.* manufactured IR-tapered fiber sensors based on $Ge_{20}Se_{80}$ with different geometries of the sensitive zone (straight, U-shaped form, one loop, two loops) to detect the content of an additive to diesel fuel and hence attained a detection limit of **0.02% (# 200ppm)**

A. P. Velmuzhov *et al.*, "Optical fibers based on special pure Ge20Se80 and Ge26As17Se25Te32 glasses for FEWS," *Journal of Non-Crystalline Solids*, vol. 517, pp. 70–75, Aug. 2019, doi: 10.1016/j.jnoncrysol.2019.04.043.

Chimie de surface et procédés thermo-électriques pour de nouvelles fonctionnalités à la surface de matériaux vitreux

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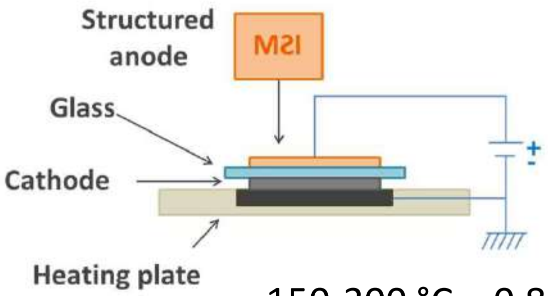
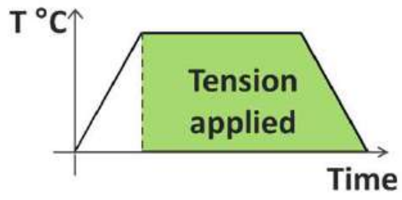
Institut de Chimie de la Matière Condensée de Bordeaux, Université de Bordeaux, 87 Avenue du Dr Schweitzer, F-33608, Pessac, France

USTV / Dijon 2024

Thermo Electrical polarization



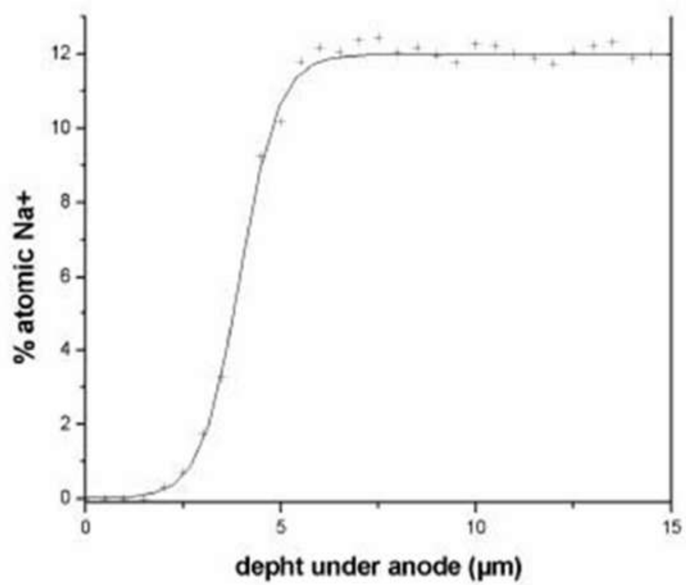


150-300 °C – 0.8-5000 V

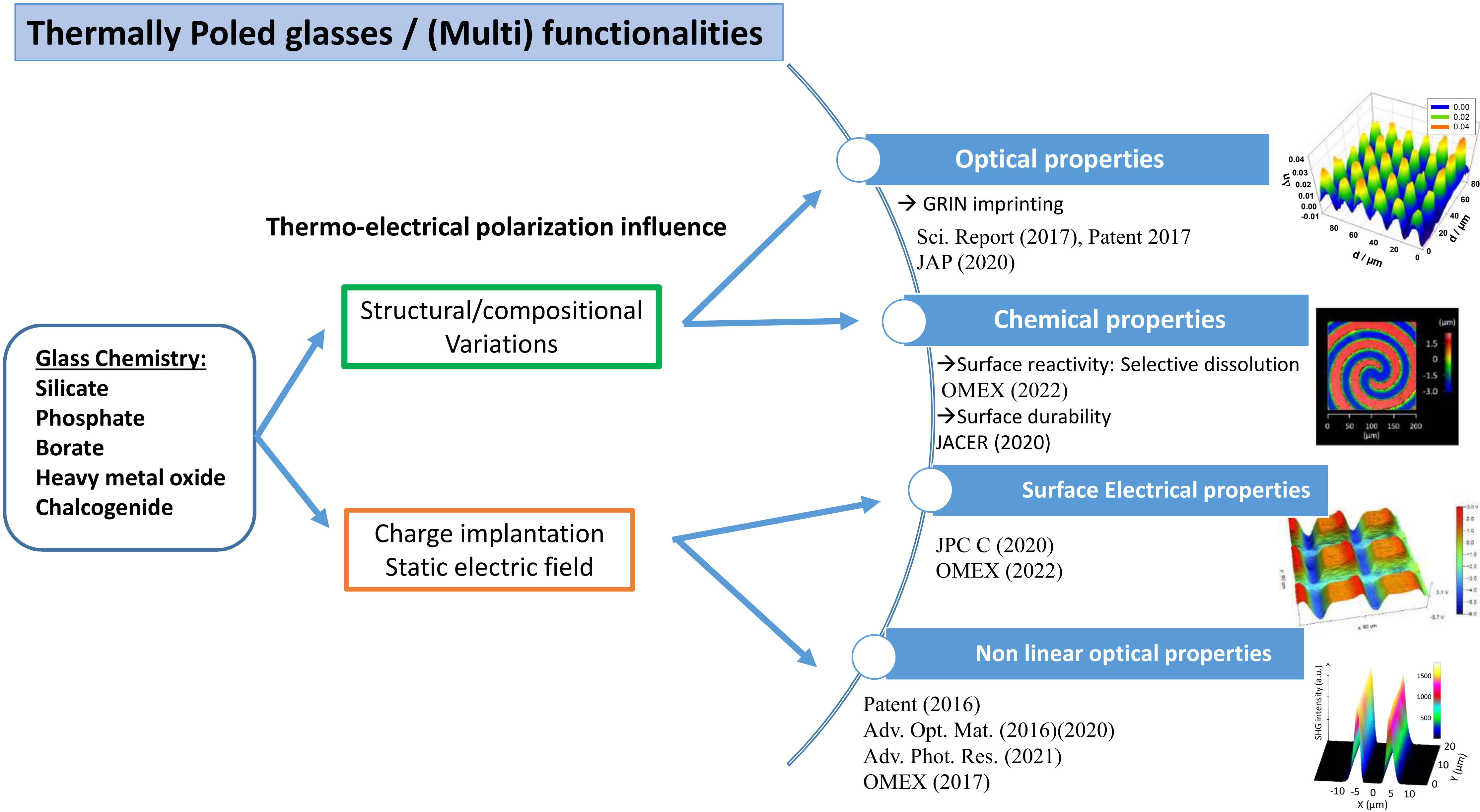
→ **Charge Dissociation**

→Mobile Cation depletion
↘**High Composition variations**
↘**Strutural modification**
→**lever for the control of the physico-chemical properties of glass**

→Static Electric Field implantation
↘ **E_{int} up to 10^8-10^9 V/m**
→**Allow second order otical properties**
$\chi^{(2)} = 3\ \chi^{(3)}.E_{int}$



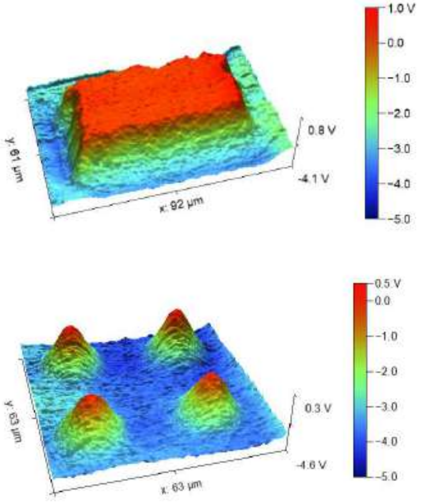
→ **Understanding and control of high field solid state electrochemical processes in glassy matrices**


Thermally Poled glasses / (Multi) functionalities
Thermo-electrical polarization influence
Glass Chemistry:
Silicate
Phosphate
Borate
Heavy metal oxide
Chalcogenide
Structural/compositional Variations
Charge implantation
Static electric field
Optical properties
→ GRIN imprinting
Sci. Report (2017), Patent 2017
JAP (2020)
Chemical properties
→Surface reactivity: Selective dissolution
OMEX (2022)
→Surface durability
JACER (2020)
Surface Electrical properties
JPC C (2020)
OMEX (2022)
Non linear optical properties
Patent (2016)
Adv. Opt. Mat. (2016)(2020)
Adv. Phot. Res. (2021)
OMEX (2017)
Δn
d / μm
SHG intensity (a.u.)
X (μm)
Y (μm)

Can we use surface electrical properties on glassy materials to influence orientation and/or conformation of molecular systems ?

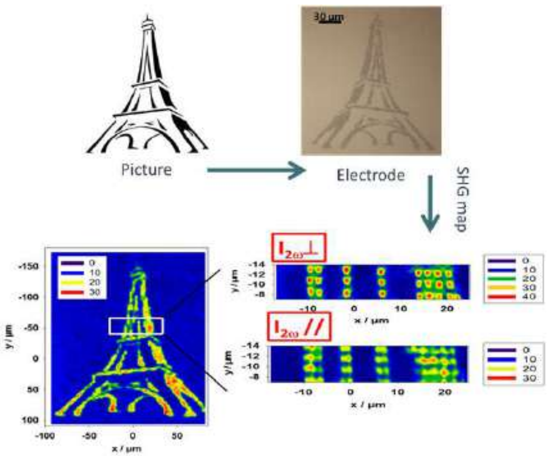
Spatial and geometry control of electrical or electro-optical effects

Surface electrical potential on a chalcogenide glass



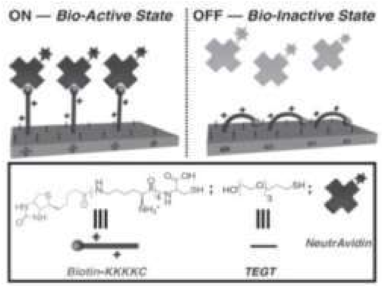
J. Phys. Chem. C (2020)

Second order optical properties



JNCS (2024)
J Phys Mater (2024)
J Mat Chem C (2022)
Adv Opt Mat. (2020)
Opt Mat Express (2018)
Adv Opt Mat. (2016)

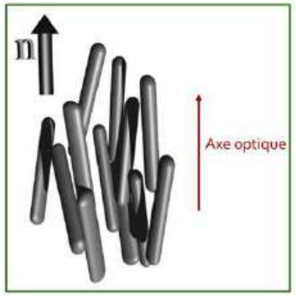
Surface chemistry on poled glassy surface

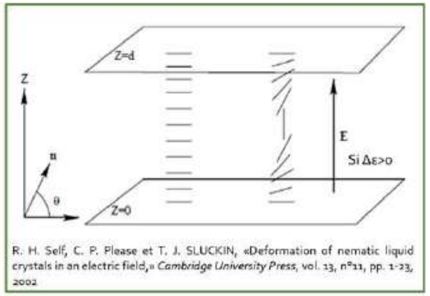


Adv. Func. Mater 2010, 20, 2657

ANR Surf Glass IR starting January 2024

Liquid Cristals on poled glassy surface





PhD A. Goillot 2022
PhD A. Maillard 2024

Research Article | Vol. 12, No. 7 / 1 Jul 2022 / Optical Materials Express 2462

Optical Materials EXPRESS

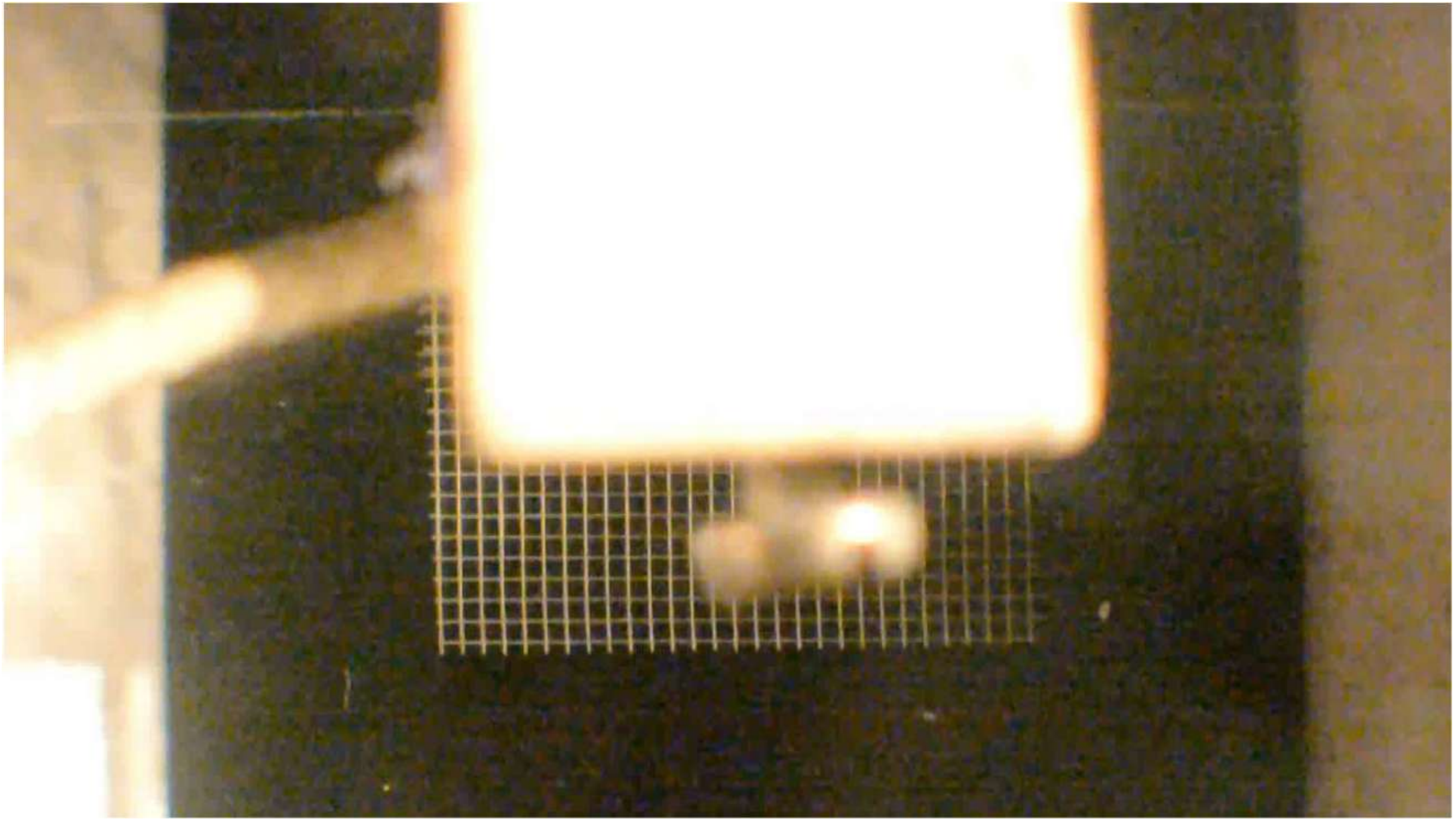
Plasma assisted micro poling of glassy surfaces: a new tool to achieve liquid crystal multi-domain alignments [Invited]

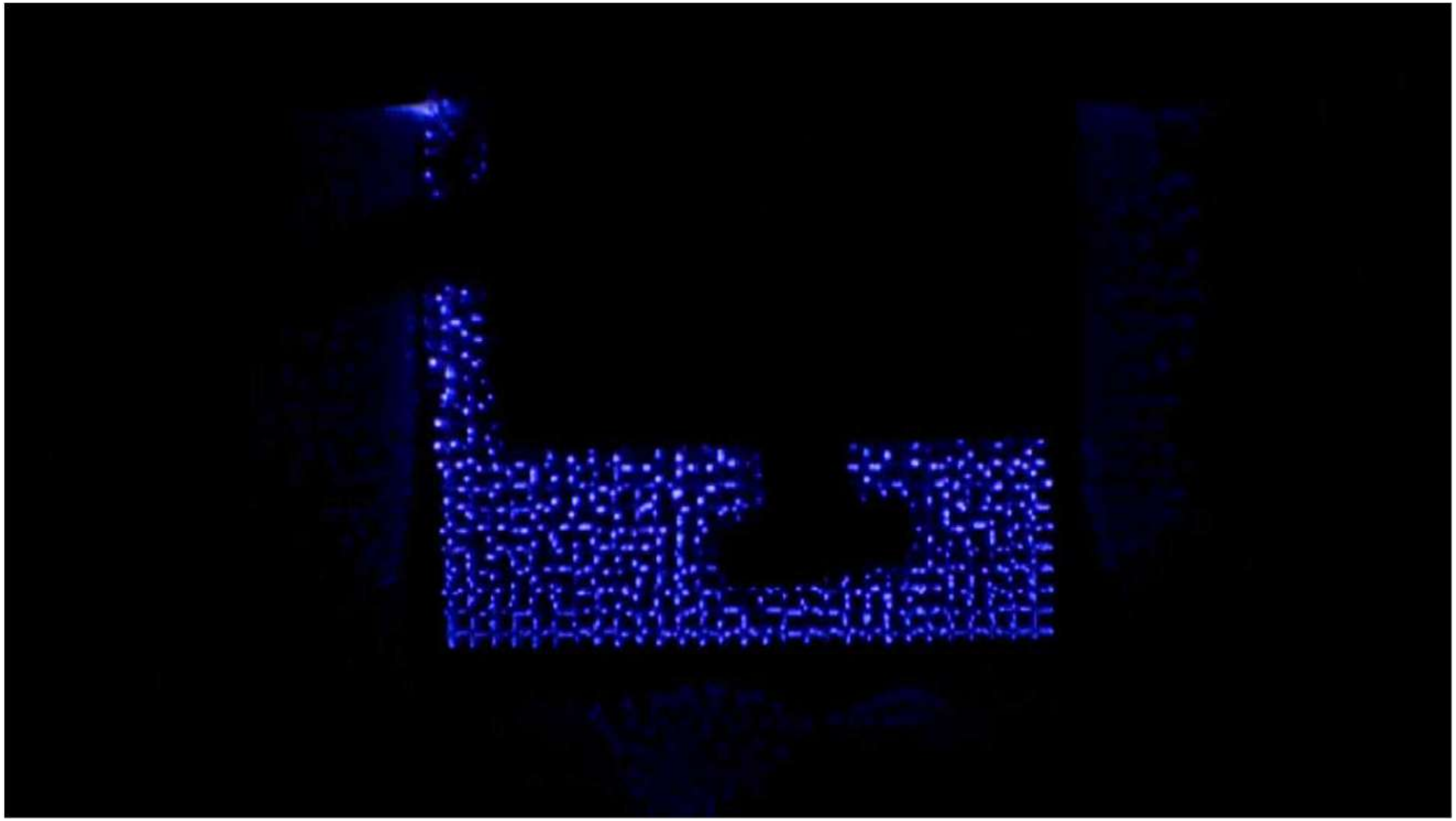
ALICE GOILLOT,[1,2] ALEXIS MAILLARD,[1,2] TIGRAN GALSTIAN,[2] YOUNÈS MESSADDEQ,[2] FREDERIC ADAMIETZ,[1] VINCENT RODRIGUEZ,[1] AND MARC DUSSAUZE[1,*]

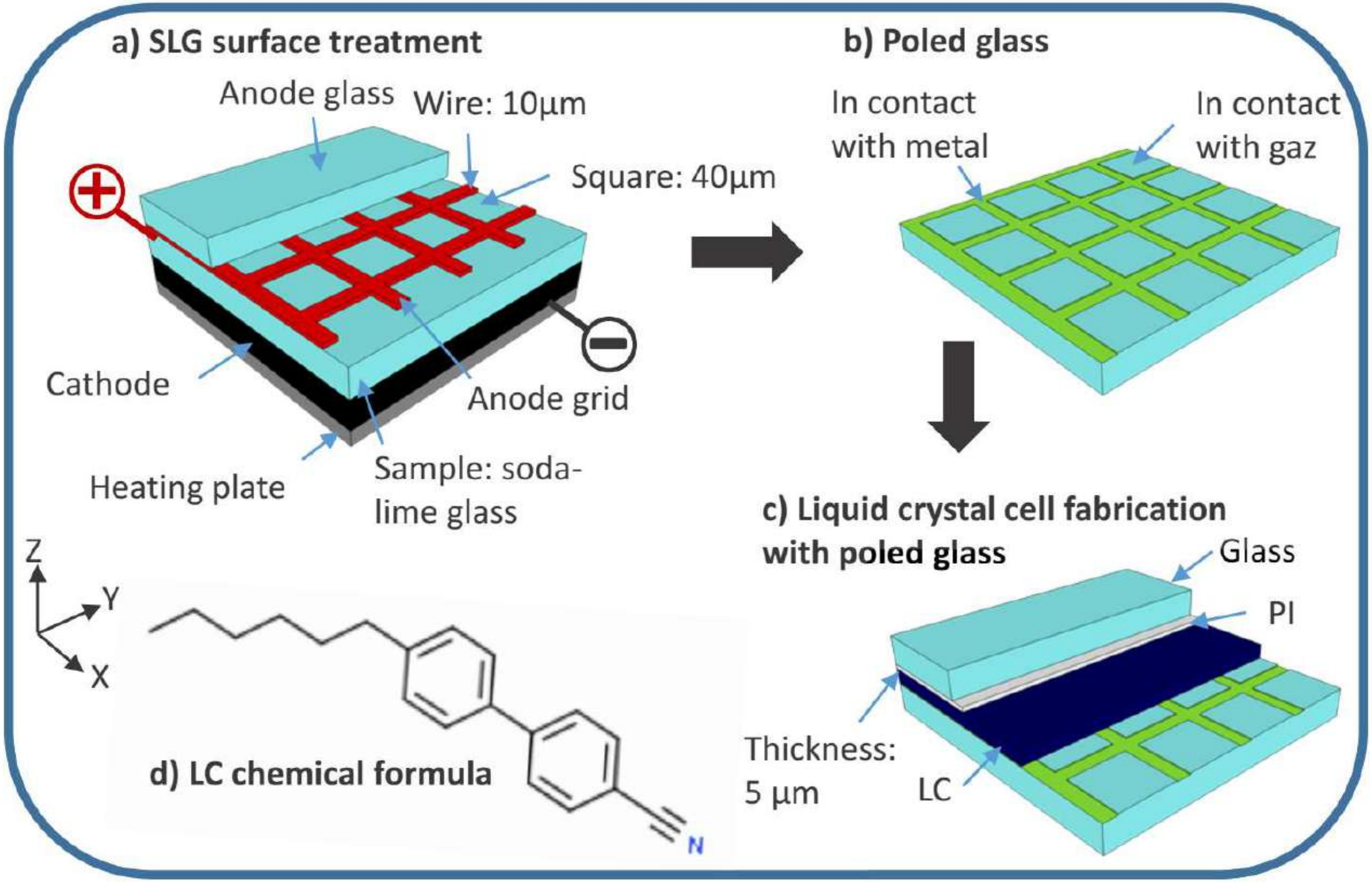
[1] *Institut des Sciences Moléculaires, UMR 5255 CNRS, Université de Bordeaux, 351 cours de la Libération, Talence Cedex 33405, France*

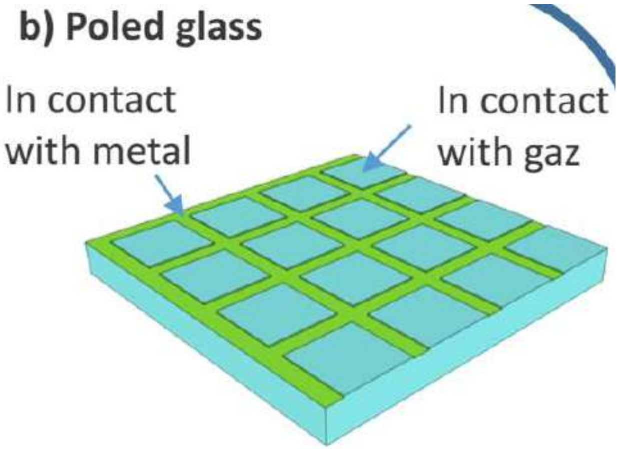
[2] *Centre d'optique, photonique et laser, Department of Physics, 2375 rue de la Terrasse, Université Laval, Québec, G1V 0A6, Canada*

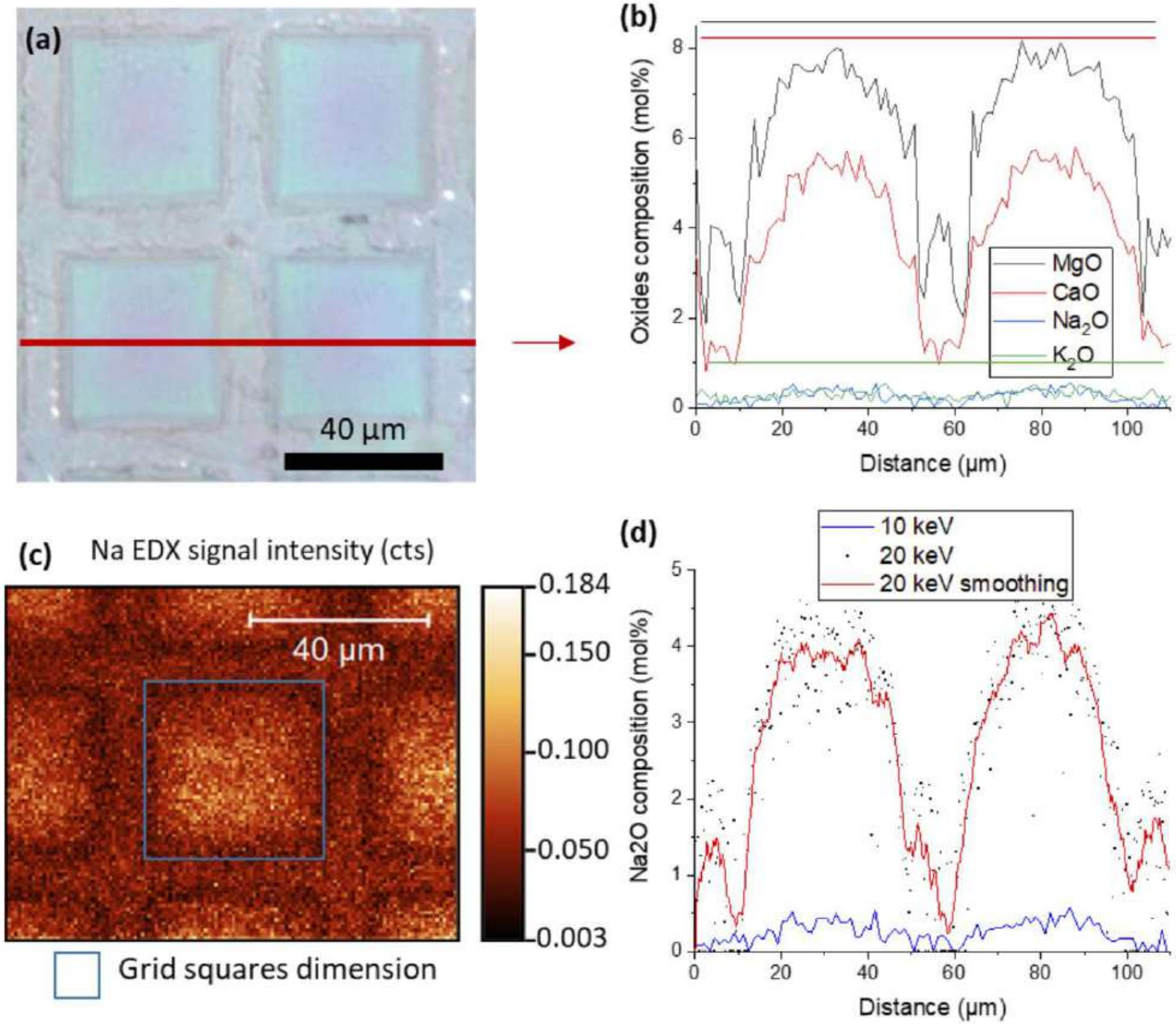
[*] *marc.dussauze@u-bordeaux.fr*

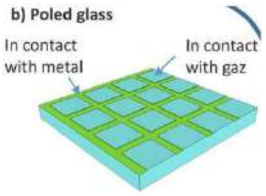





a) SLG surface treatment
Anode glass
Wire: 10µm
Square: 40µm
Cathode
Anode grid
Heating plate
Sample: soda-lime glass
b) Poled glass
In contact with metal
In contact with gaz
c) Liquid crystal cell fabrication with poled glass
Glass
PI
Thickness: 5 µm
LC
Z
Y
X
d) LC chemical formula
N


b) Poled glass
In contact with metal
In contact with gaz

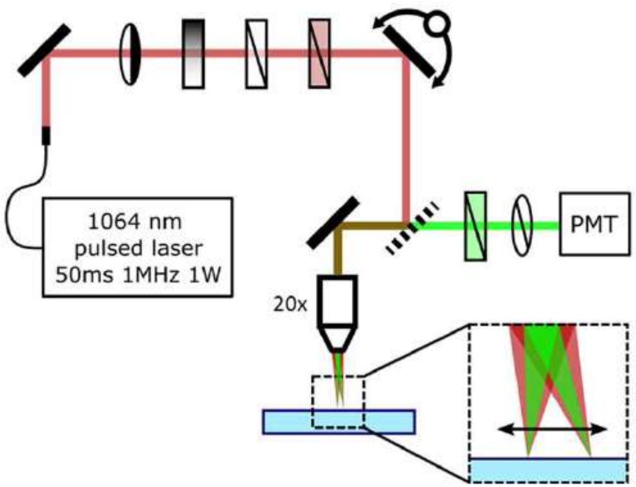

(a)
40 µm
(b)
Oxides composition (mol%)
Distance (µm)
MgO
CaO
Na2O
K2O
(c)
Na EDX signal intensity (cts)
40 µm
0.184
0.150
0.100
0.050
0.003
Grid squares dimension
(d)
10 keV
20 keV
20 keV smoothing
Na2O composition (mol%)
Distance (µm)

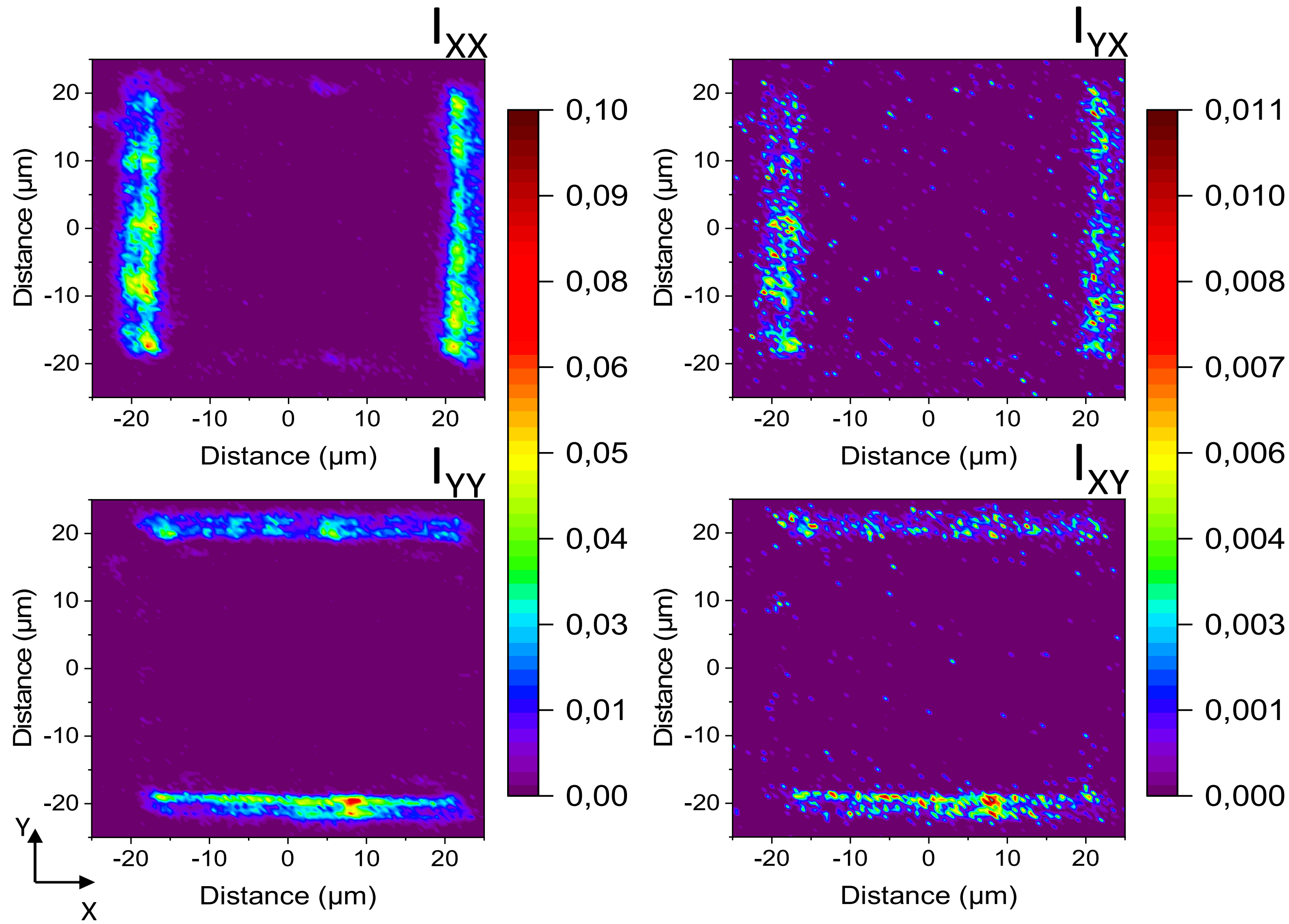


Electric Field Induced Second Harmonic (EFISH)

$$\chi^{(2)}(-\omega_2;\omega_1,\omega_1) = 3\,\chi^{(3)}(-\omega_2;\omega_1,\omega_1,0)\,\boldsymbol{E}_{stat}$$

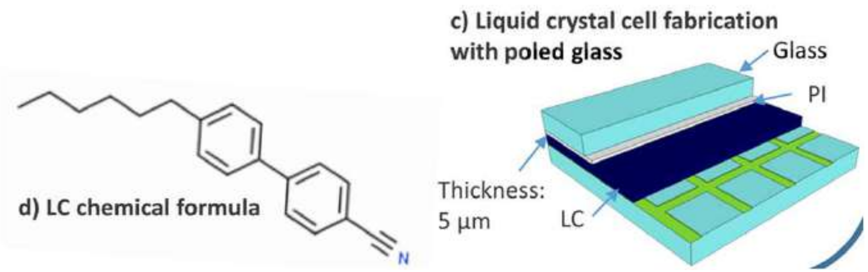
$$\omega_2 = 2\omega_1$$

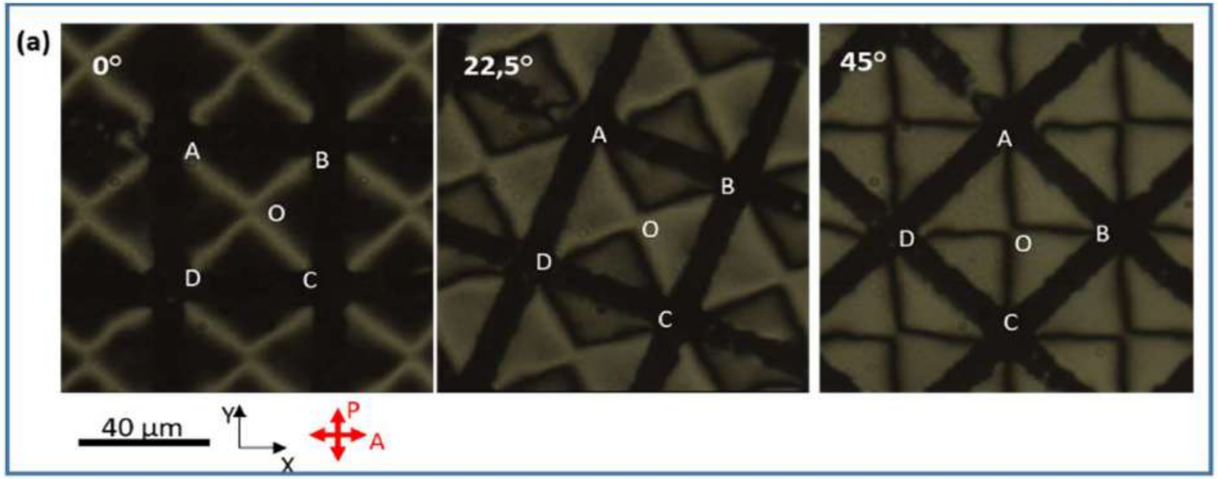


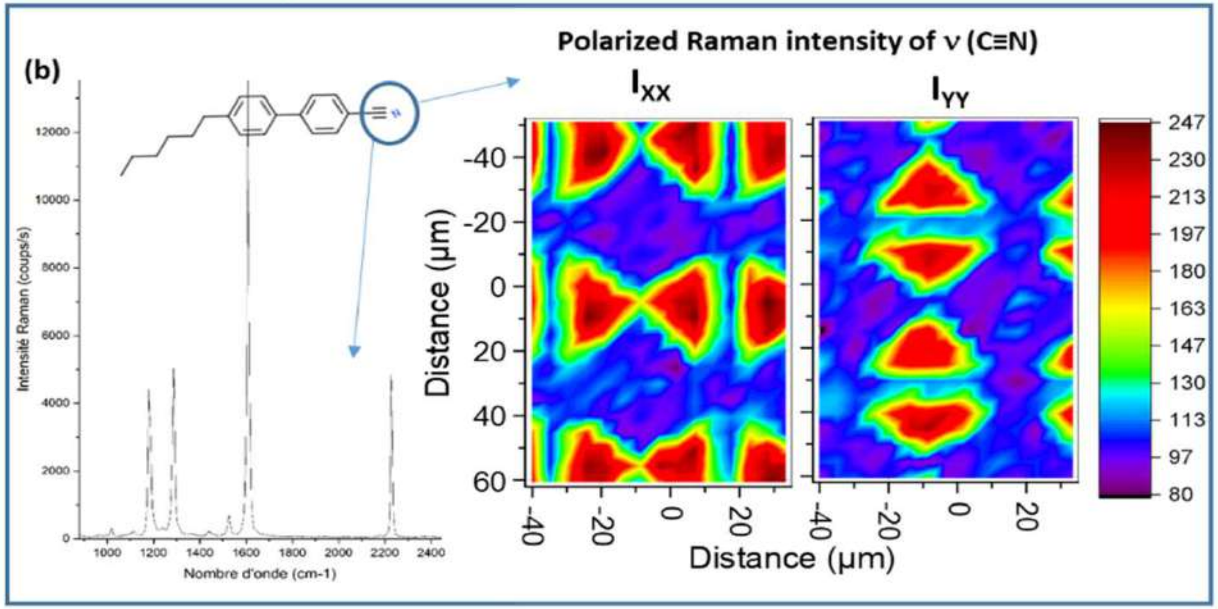


Spatial and geometry control of the embedded static electric field

Plasma assisted micro poling of glassy surfaces: a new tool to achieve liquid crystal multi-domain alignments



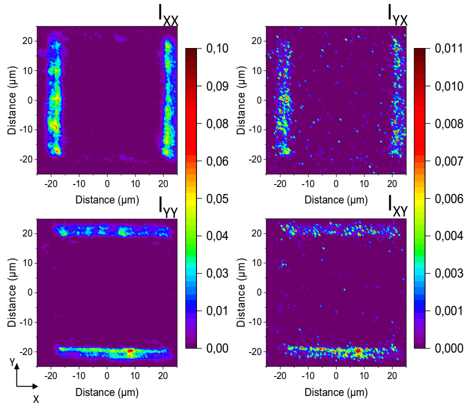


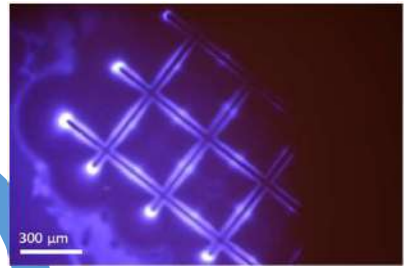


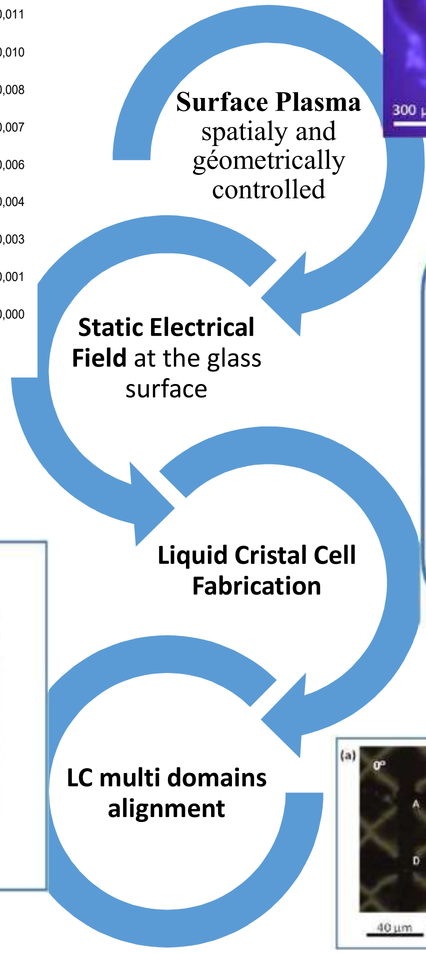
Thèse Alice Goillot, Alexis Maillard
Collaboration COPL Quebec
OMEX 12 (7) 2022, 2462
Patent 2022

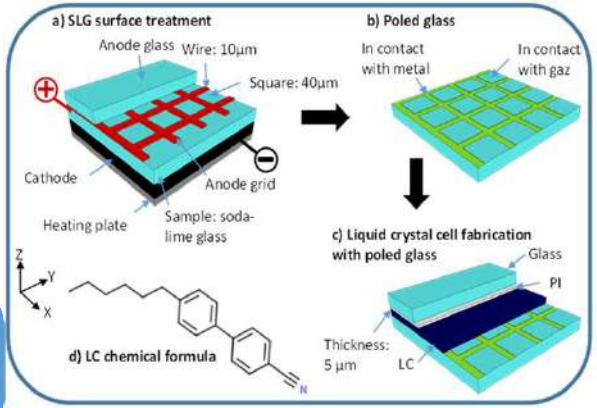
PLASMA ASSISTED MICRO POLING OF GLASSY SURFACES: A NEW TOOL TO ACHIEVE LIQUID CRYSTAL MULTI-DOMAIN ALIGNMENTS

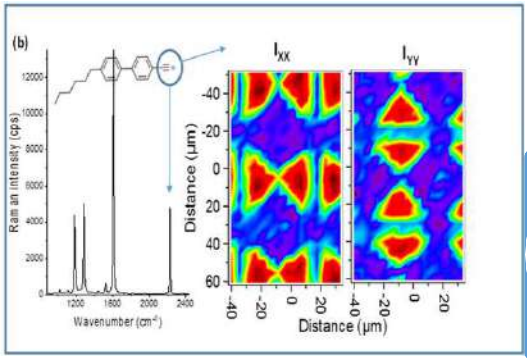
Thèse Alice Goillot, Alexis Maillard
Collaboration COPL Quebec
OMEX 12 (7) 2022, 2462
Patent 2022

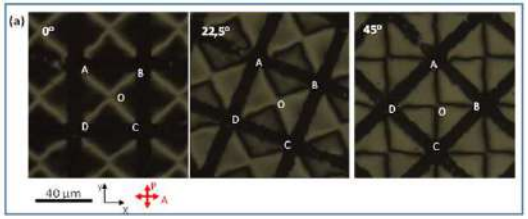












Thank you for your attention !

My close collaborators:

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