SUSTAINABLE FUNCTIONALIZATION OF sp^2 CARBON ALLOTROPES AS FILLERS FOR RUBBER COMPOUNDS WITH LOWER DISSIPATION OF ENERGY

Vincenzina Barbera

A. Bernardi, D. Locatelli, G. Prioglio, C. Pennetta, L. Rubino, M. Galimberti

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

Items of the presentation

- Strategy of Research
- C-3 building blocks
- Valorization:
  - functionalization of carbon allotropes
  - reinforcement of diene elastomers

ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

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Strategy of Research

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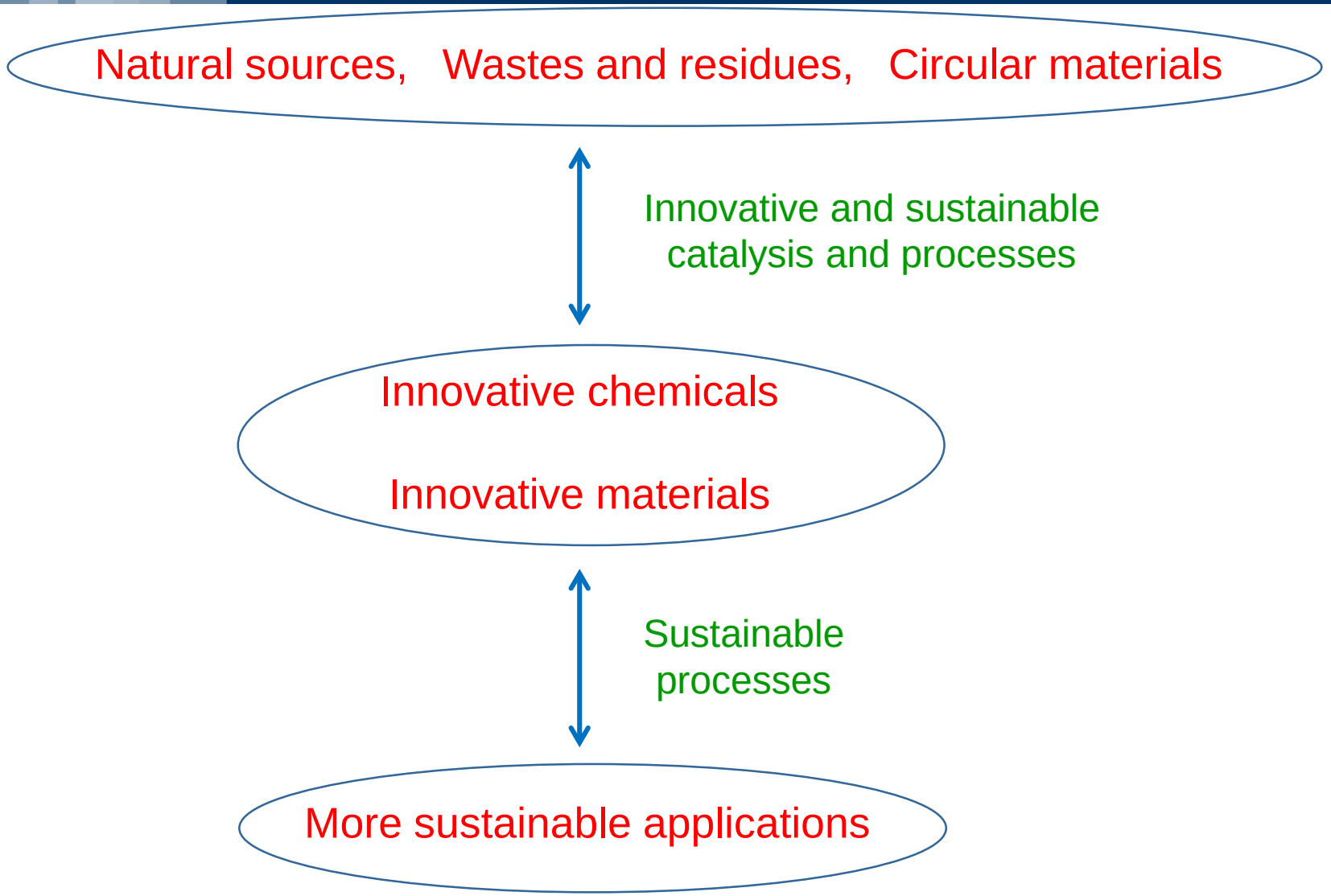
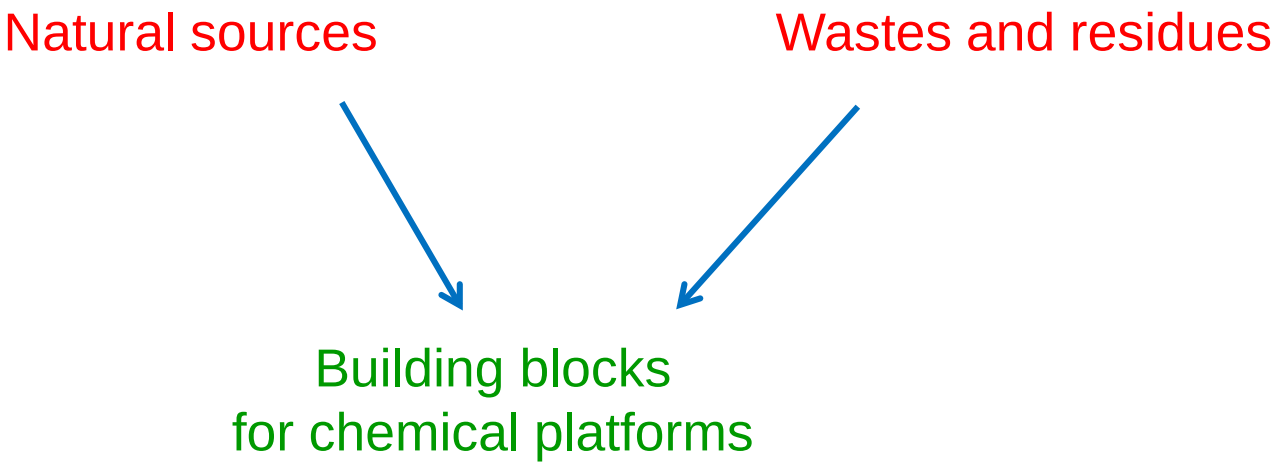
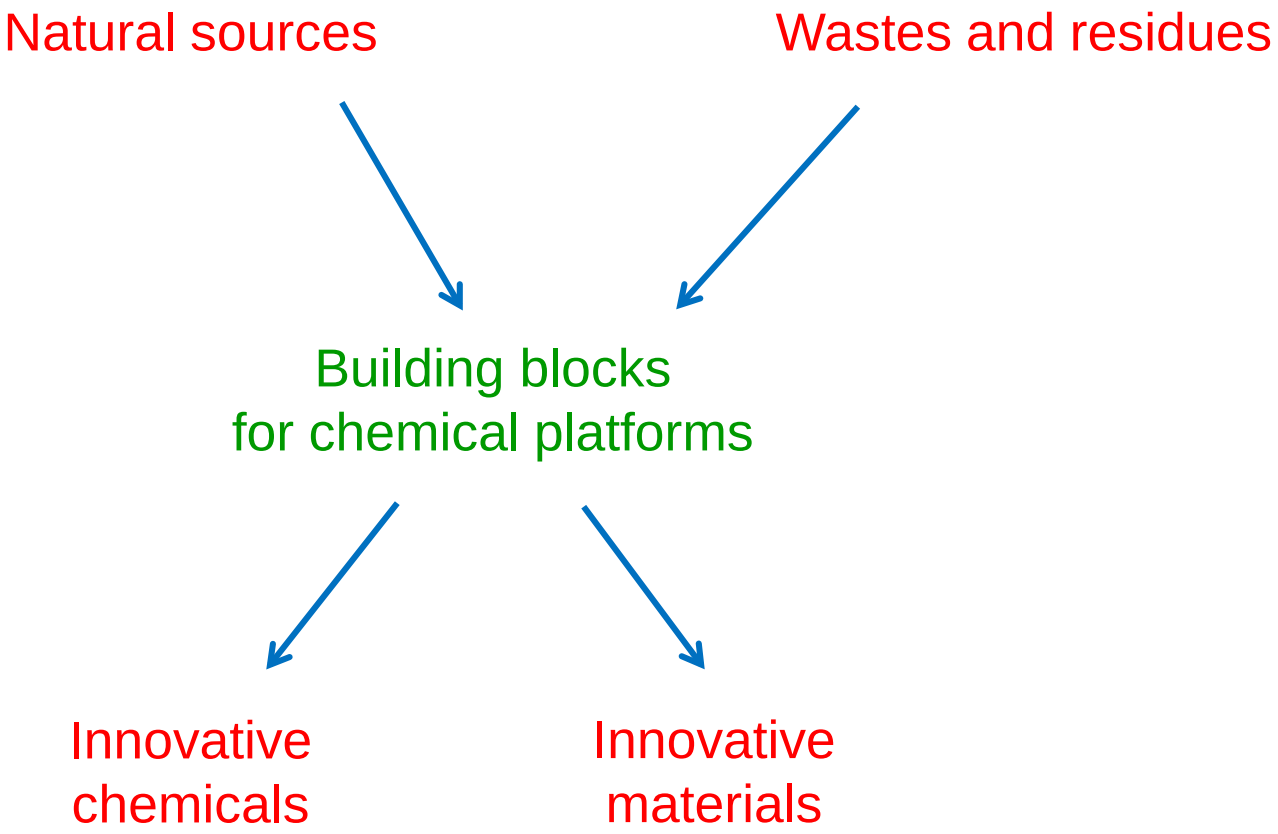
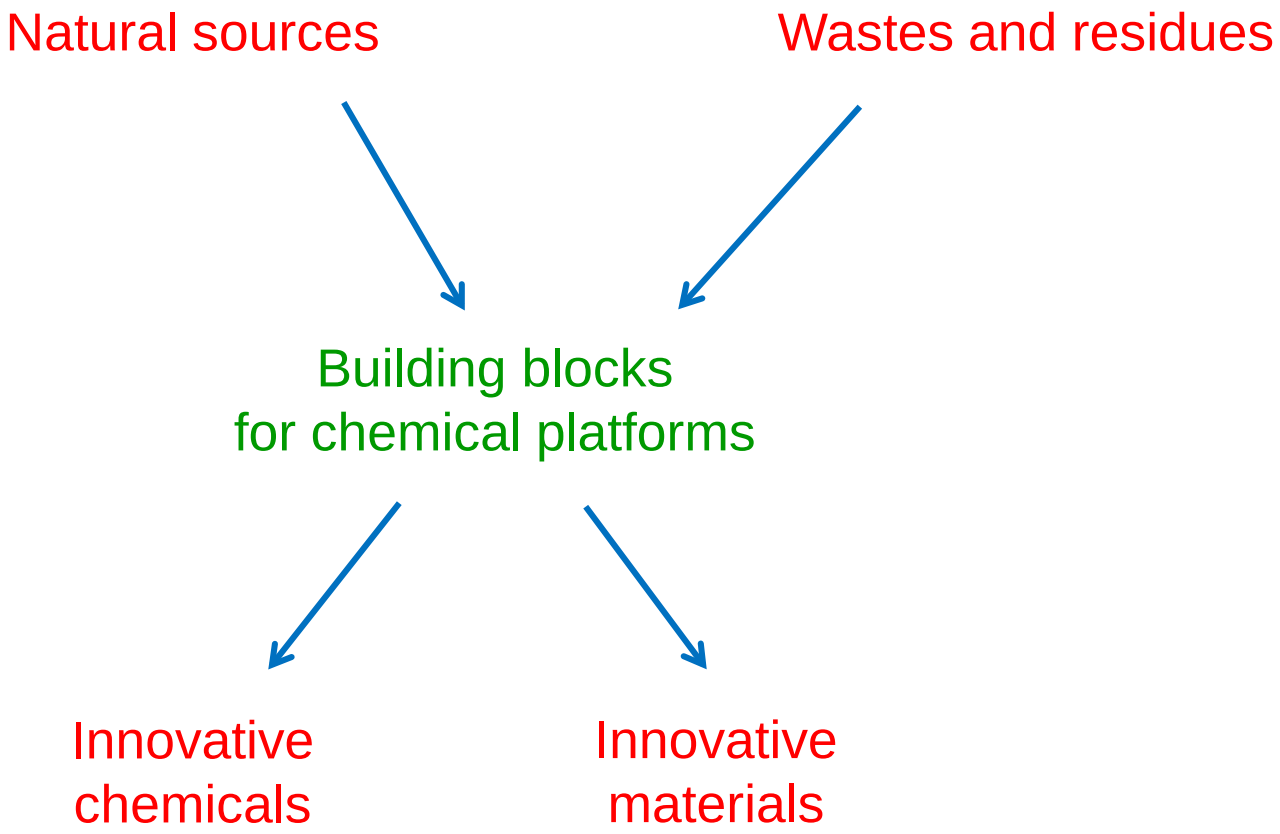
Strategy: sustainability for innovation



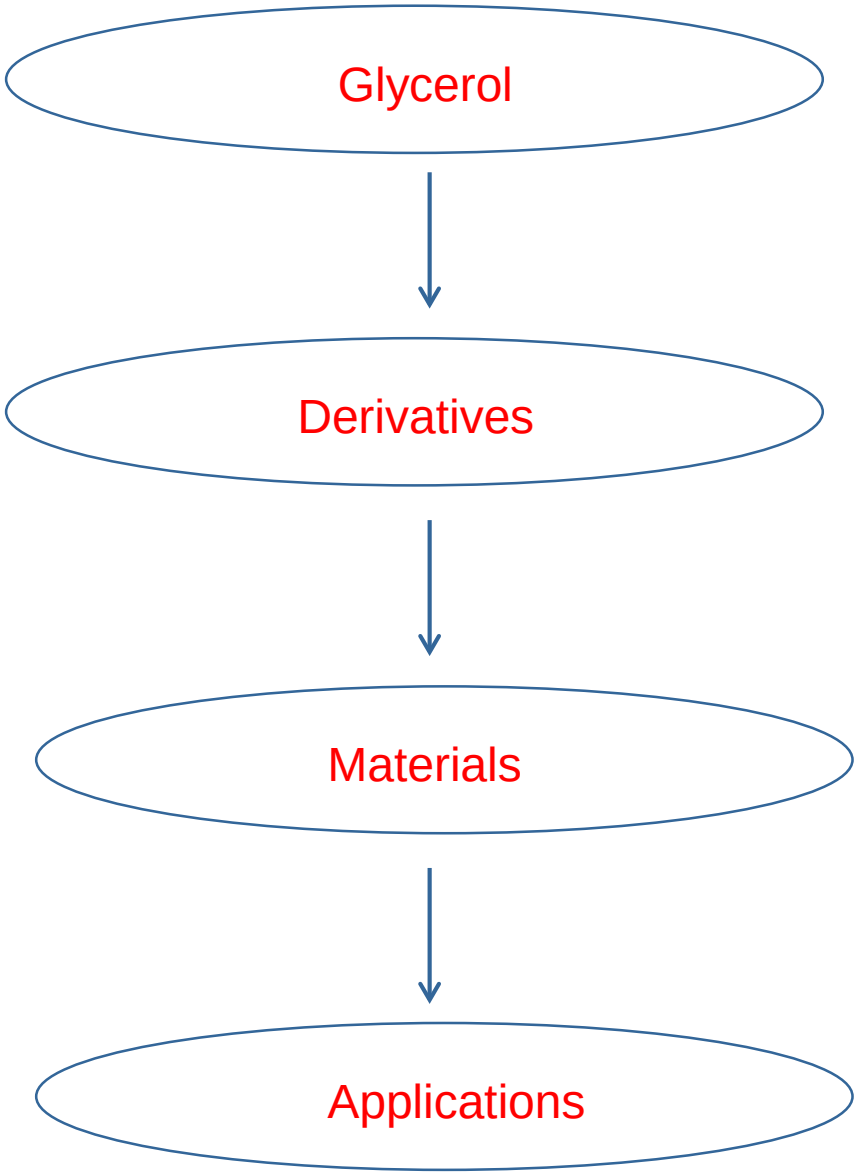

Natural sources
Wastes and residues
Building blocks
for chemical platforms


Natural sources
Wastes and residues
Building blocks
for chemical platforms
Innovative
chemicals
Innovative
materials

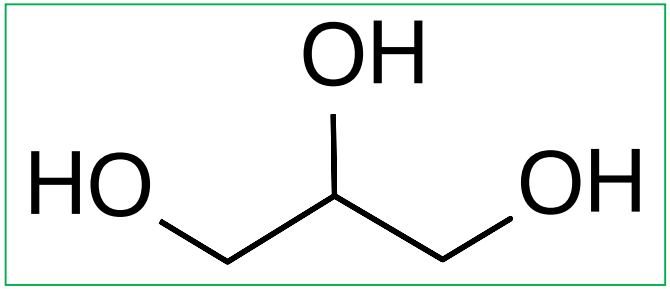


☞ Chemicals, Additives, Modifiers, Polymers

The ISCaMaP Group. One example



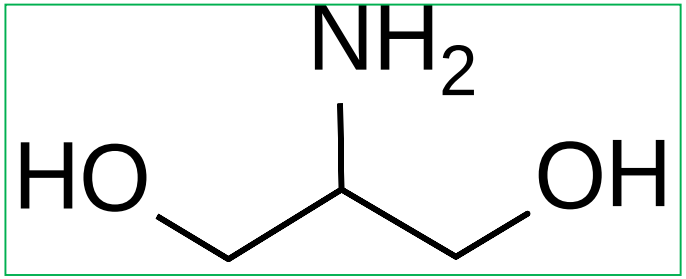
Glycerol



IUPAC: propane-1,2,3-triol
Formula: $C_3H_8O_3$
92.09 Da

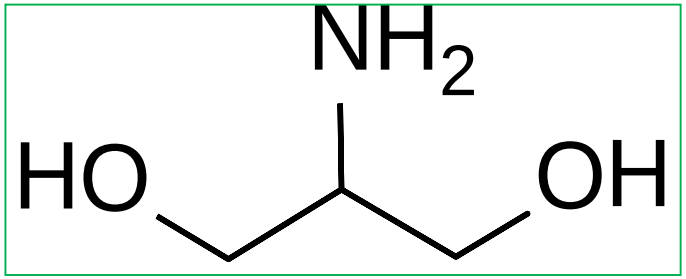
- easily available, cheap raw material
- main by-product of bio-diesel production
- not toxic
- biodegradable

Selection of the building block: serinol



- Starting building block for many reaction pathways: many derivatives
- Chemoselectivity

Selection of the building block: serinol



- Starting building block for many reaction pathways: many derivatives

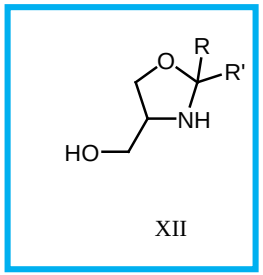
- Chemoselectivity

Reactions of the amino group with carbonyl compounds

Specific reactions of serinol with carbonyl compounds.

Without steric hindrance

and aromatic substituents

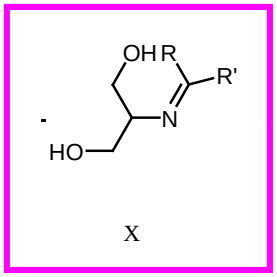


XII

Oxazolidines

With steric hindrance

and aromatic substituents

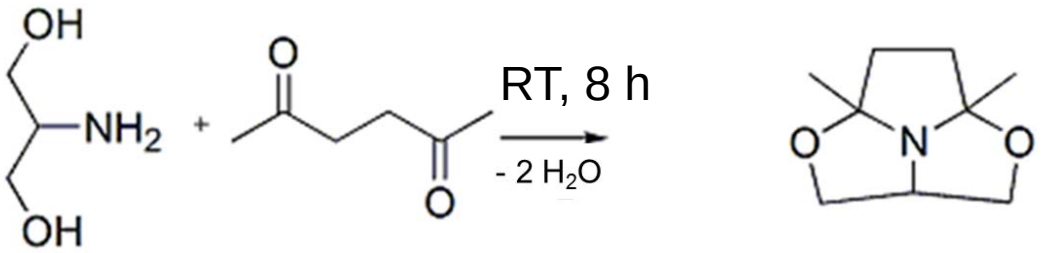


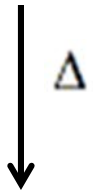
X

Imines

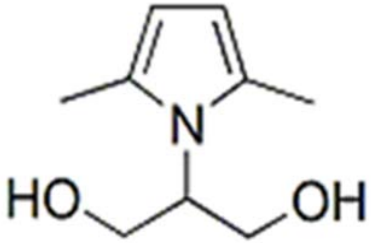
Barbera, V., Musto, S., Infortuna, G., Cipolletti, V., Citterio, A., Sun, S. and Galimberti, M., 2018. Rubber Chemistry and Technology, 91(4), pp.701-718,

Reaction of serinol with dicarbonyl compound





180°C, 3 h

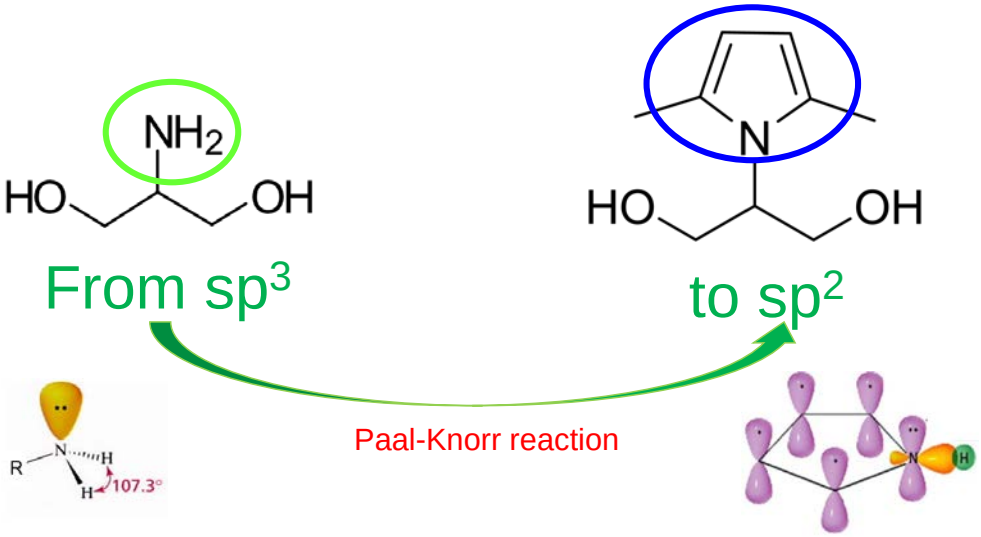


Serinol pyrrole - SP

2-(2,5-dimethyl-1*H*-pirrol-1-yl) -1,3-propanediol

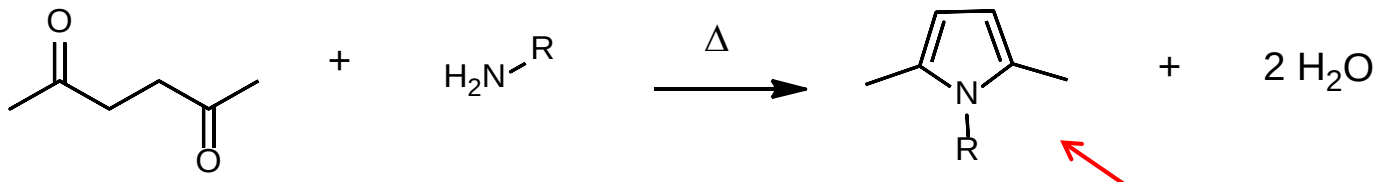
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*
M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.*, 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti,, *eXPRESS Polymer Letters* 2016, *10* (7) 548–558

Neat synthesis of Serinol pyrrole



- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

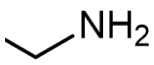
Pyrrole compounds (PyC) from neat Paal Knorr reaction



Same reaction conditions used for SP

PyC

Yield %



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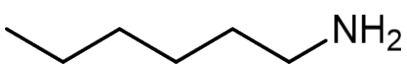

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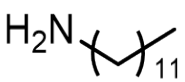

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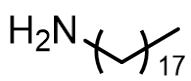

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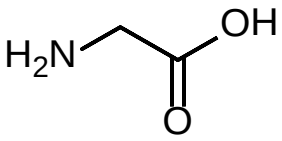

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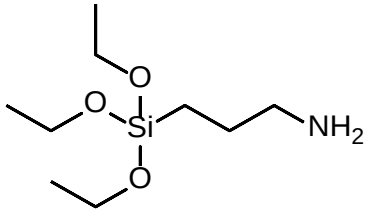

70

V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Objectives of the research activity

- To functionalize various carbon allotropes with a sustainable, facile, versatile method, preserving the sp^2 hybridization

- To reduce the synthetic footprint in carbon allotropes functionalization

- To prepare tailor made materials, in view of the final application

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  with a sustainable, facile, versatile method,
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- To prepare tailor made materials,
  in view of the final application: reinforcement of diene elastomers

Functionalization of sp^2 carbon allotropes

Playing with chemistry on sp^2 carbon allotropes

Carbon fillers from a layer of sp^2-bonded carbon atoms

graphene

stacked

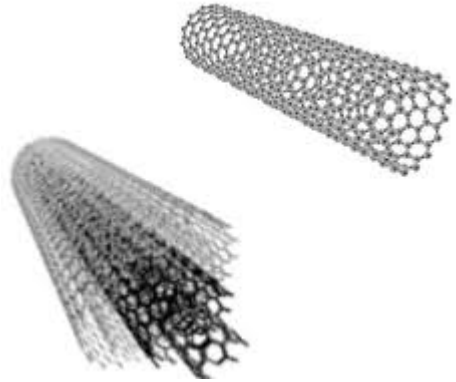
wrapped

stacked graphene layers

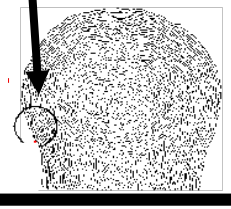
randomly arranged

with different shape anisotropy

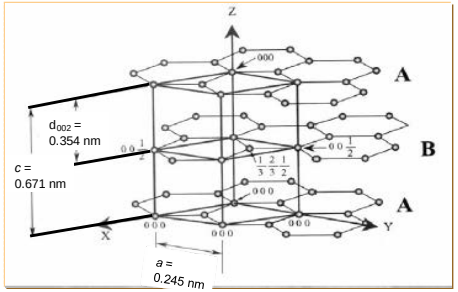
CNT



carbon black

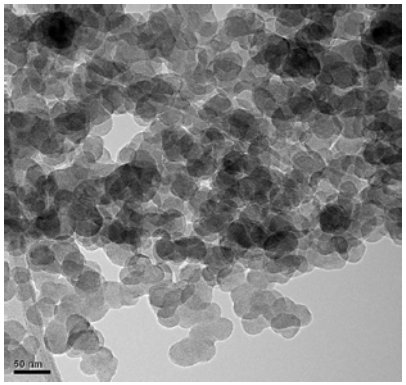


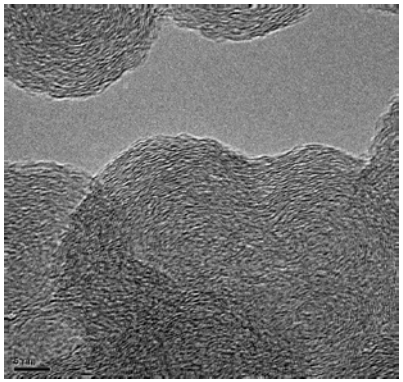
graphite, nano-graphite, graphene



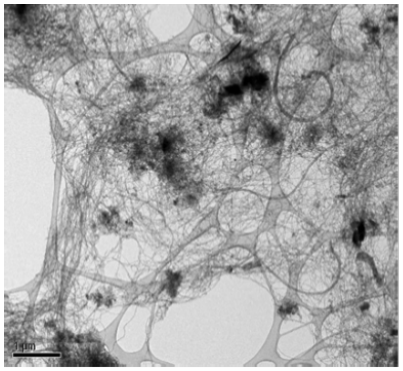
Carbon allotropes (CA)

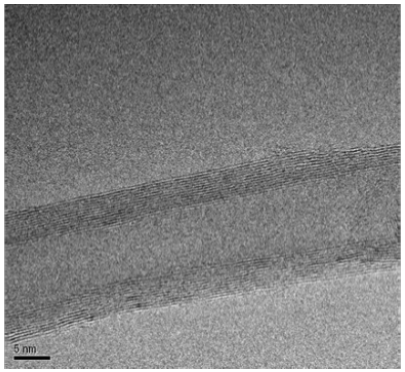
CB



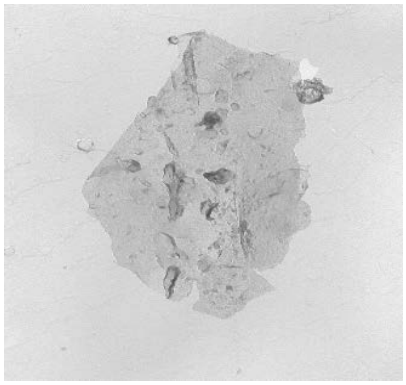


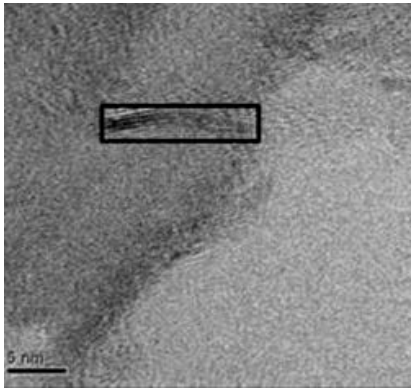
CNT





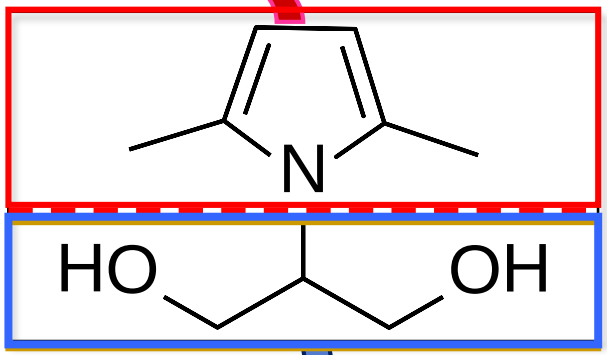
FEW LAYERS GRAPHENE





Serinolpyrrole: *Janus* molecule

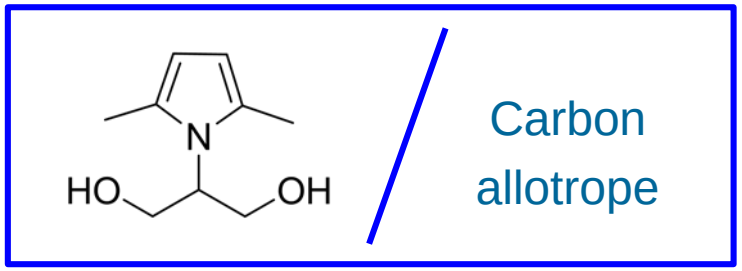
INTERACTION WITH LIPOPHILIC MATRIX AND GRAPHITIC CARBONS



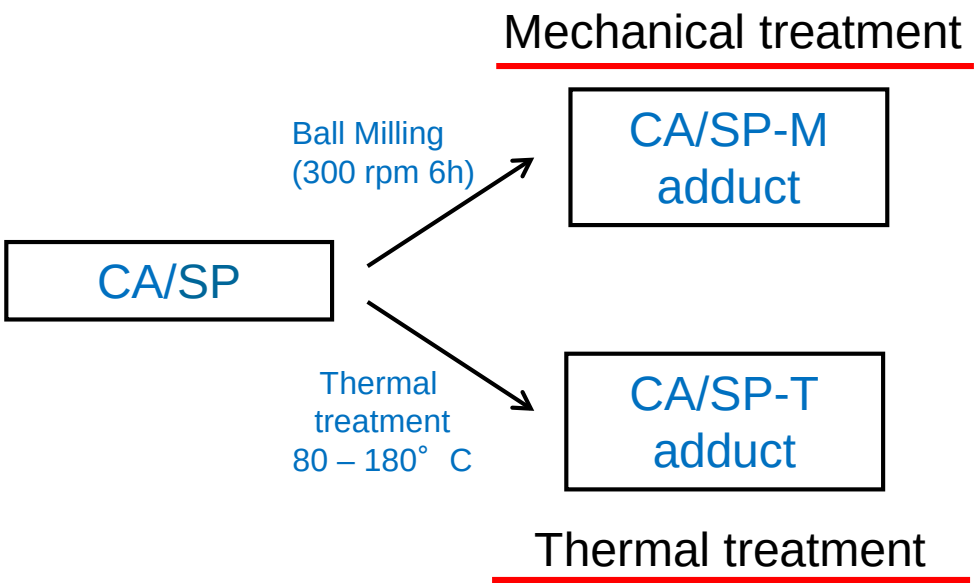
REACTIONS WITH FUNCTIONAL GROUPS

INTERACTION WITH POLAR SURROUNDING

Adducts of SP with CA - Preparation

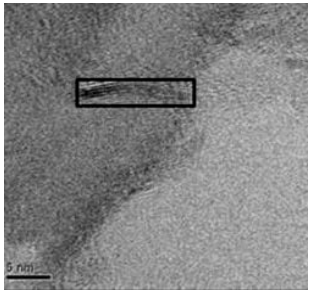
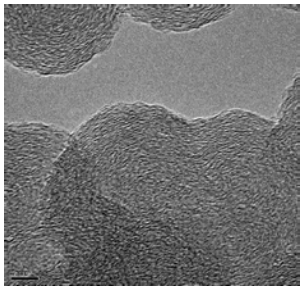
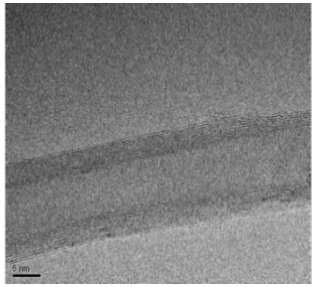


CA-SP



Barbera, V., Citterio, A., Galimberti, M., Leonardi, G., Sebastiano, R., Shisodia, S.U., Valerio A.M. WO 2015 189411 A1
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

High yield functionalization!

BET Surface area: [m^2/g]	**300**	**77**	**275**
Initial functional groups: [mmol/g]	**1.7**	**0.9**	**2.0**
Yields (%)*:	**96**	**82**	**92**

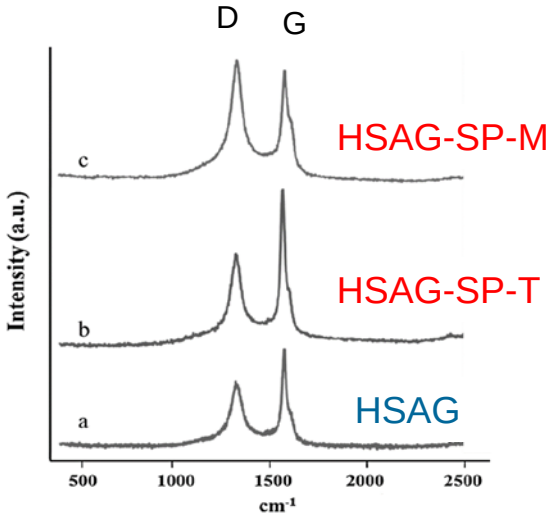
*was estimated through:

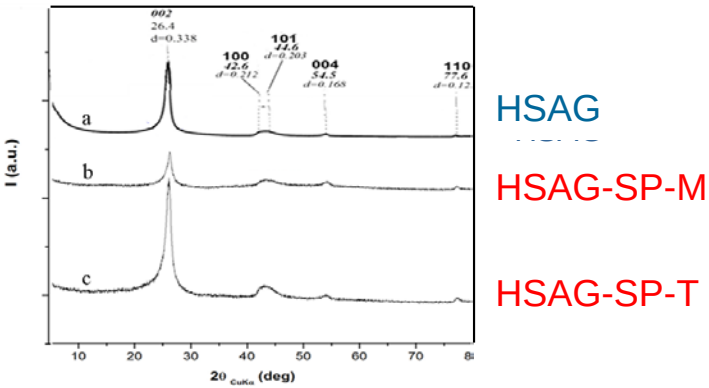
$$\text{Functionalization Yield } (\%) = 100 * \frac{\text{SP mass \% in (CA–SP adduct) after acetone washing}}{\text{SP mass \% in (CA–SP adduct) before acetone washing}}$$

Galimberti, M., Barbera, V., Sebastiano, R., Citterio, A., Leonardi, G. WO/2016/050887 A1 (2016)

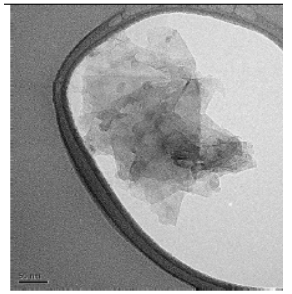
Adducts of SP with HSAG

- Functional groups up to 20%
- In plane order substantially unaltered
- No expansion of interlayer distance





Few layers graphene



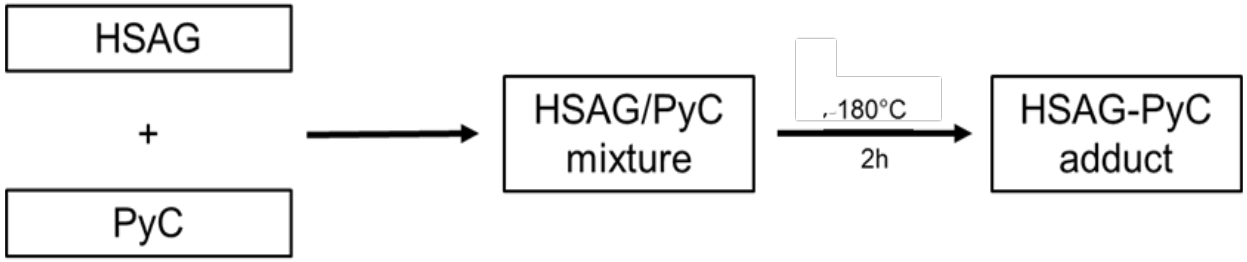
From water suspension

Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis

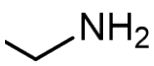
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio WO 2016 050887 A1

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, *RSC Adv.*, 2015, 5, 81142-81152

HSAG / PyC adducts



Functionalization Yield %



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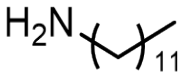
87



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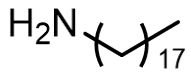

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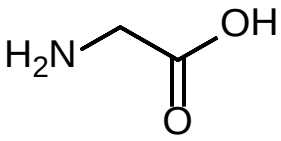

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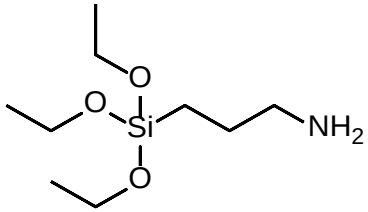

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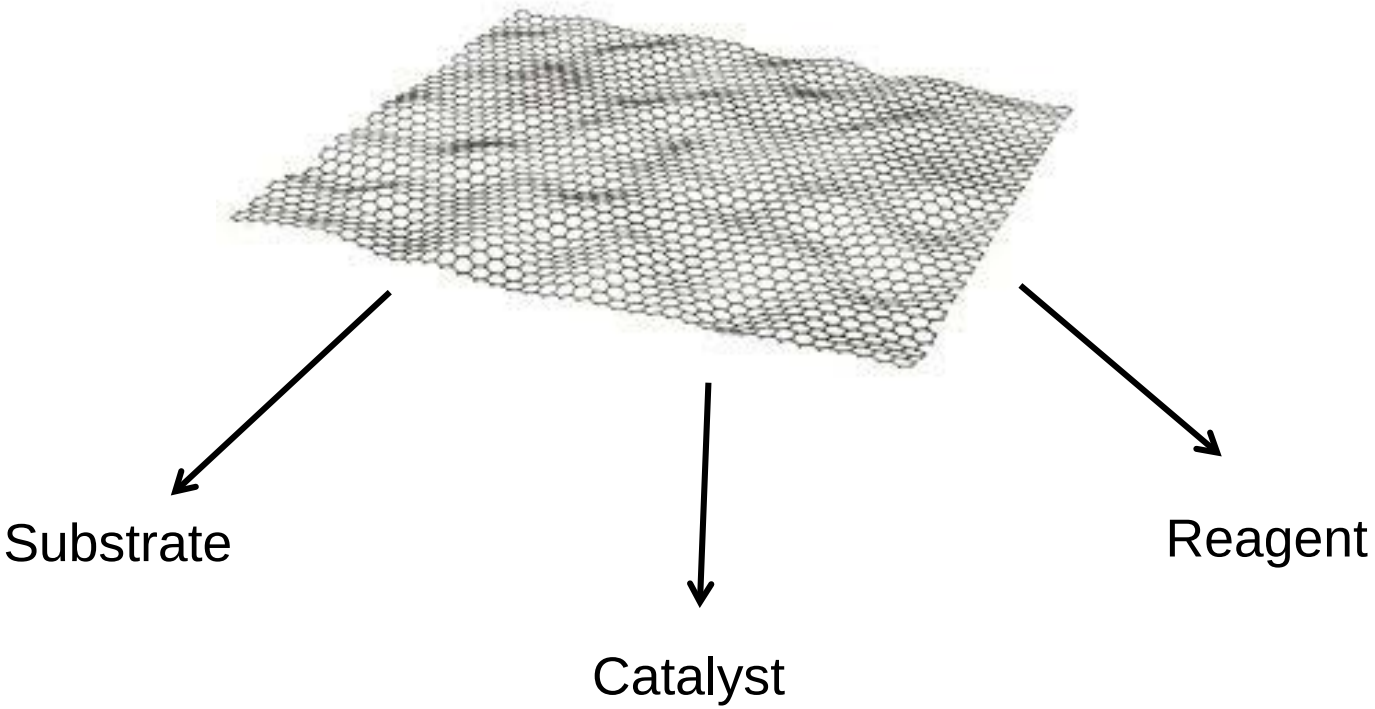
Mechanicistic considerations

Playing with chemistry on sp^2 carbon allotropes

Manifold role for the carbon allotrope



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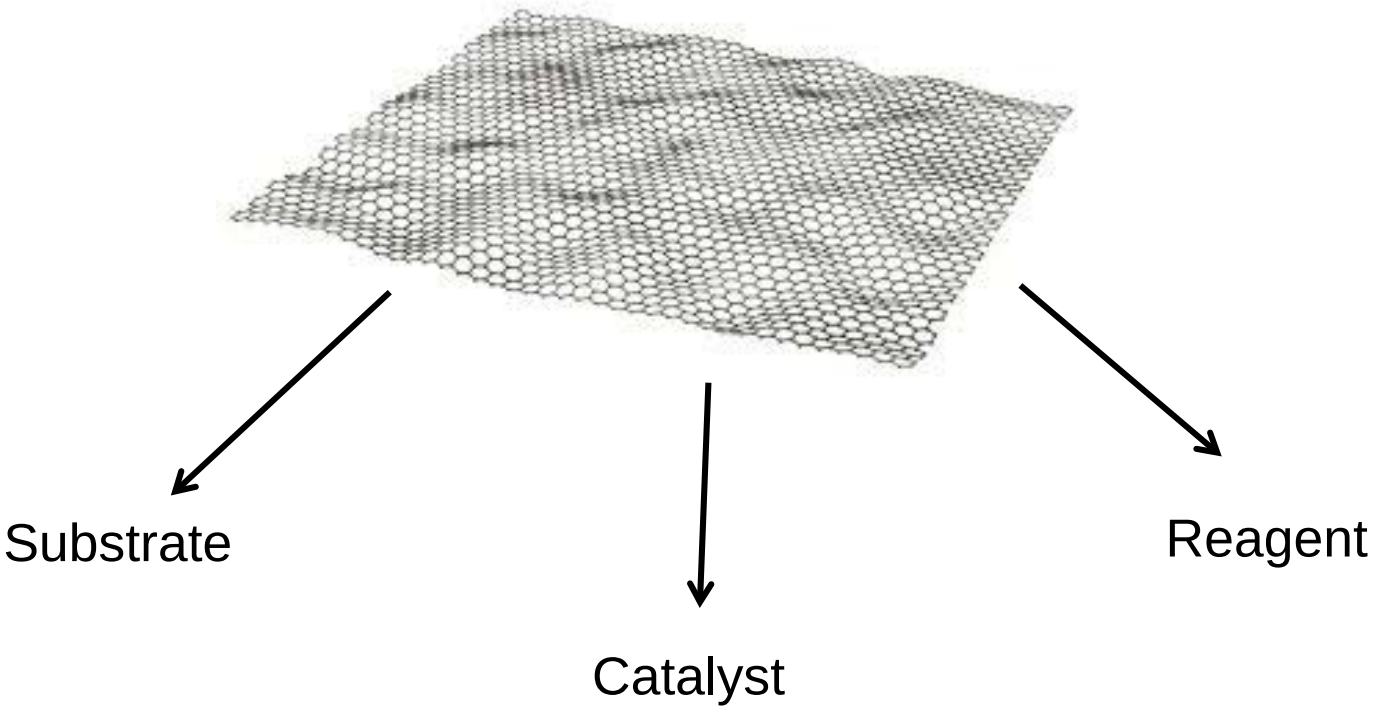
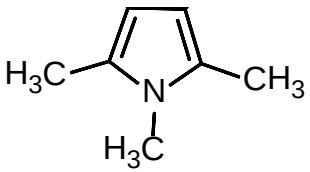


Investigation of mechanisms

Mechanism of the functionalization reaction

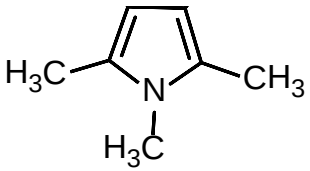
Investigation with a model compound



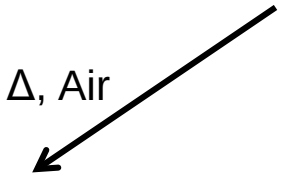
1,2,5-Trimethylpyrrole
(TMP)

Mechanism of the functionalization reaction

Investigation with a model compound

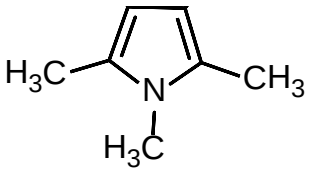


1,2,5-Trimethylpyrrole
(TMP)

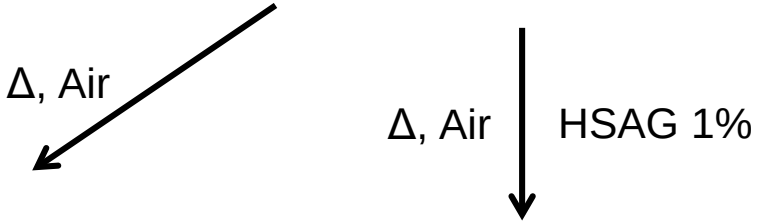


Mechanism of the functionalization reaction

Investigation with a model compound

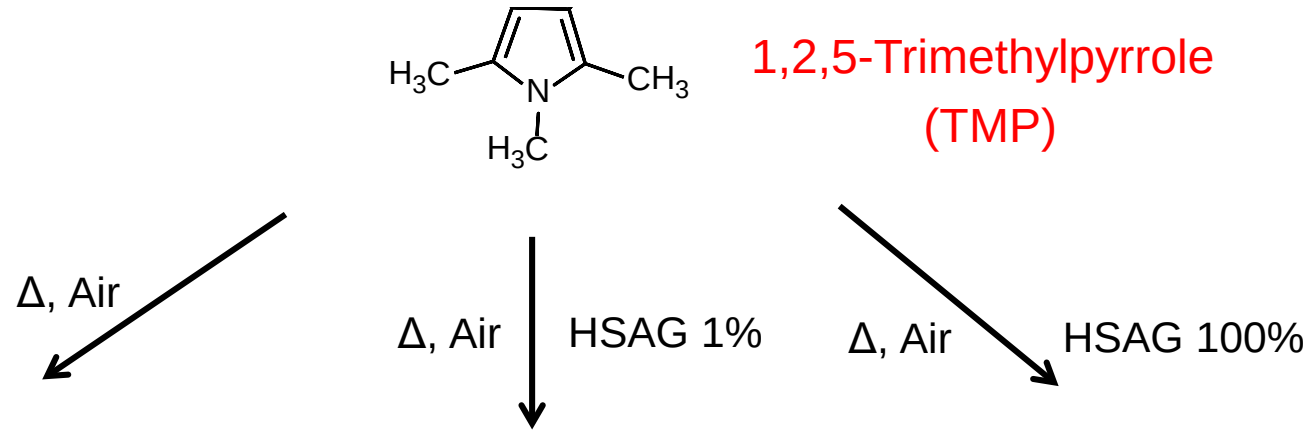


1,2,5-Trimethylpyrrole
(TMP)



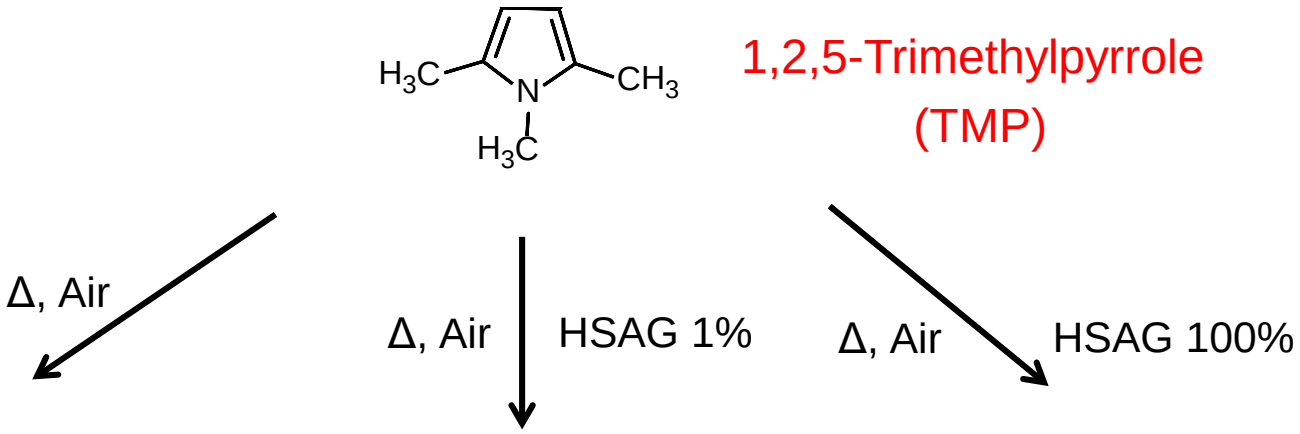
Mechanism of the functionalization reaction

Investigation with a model compound



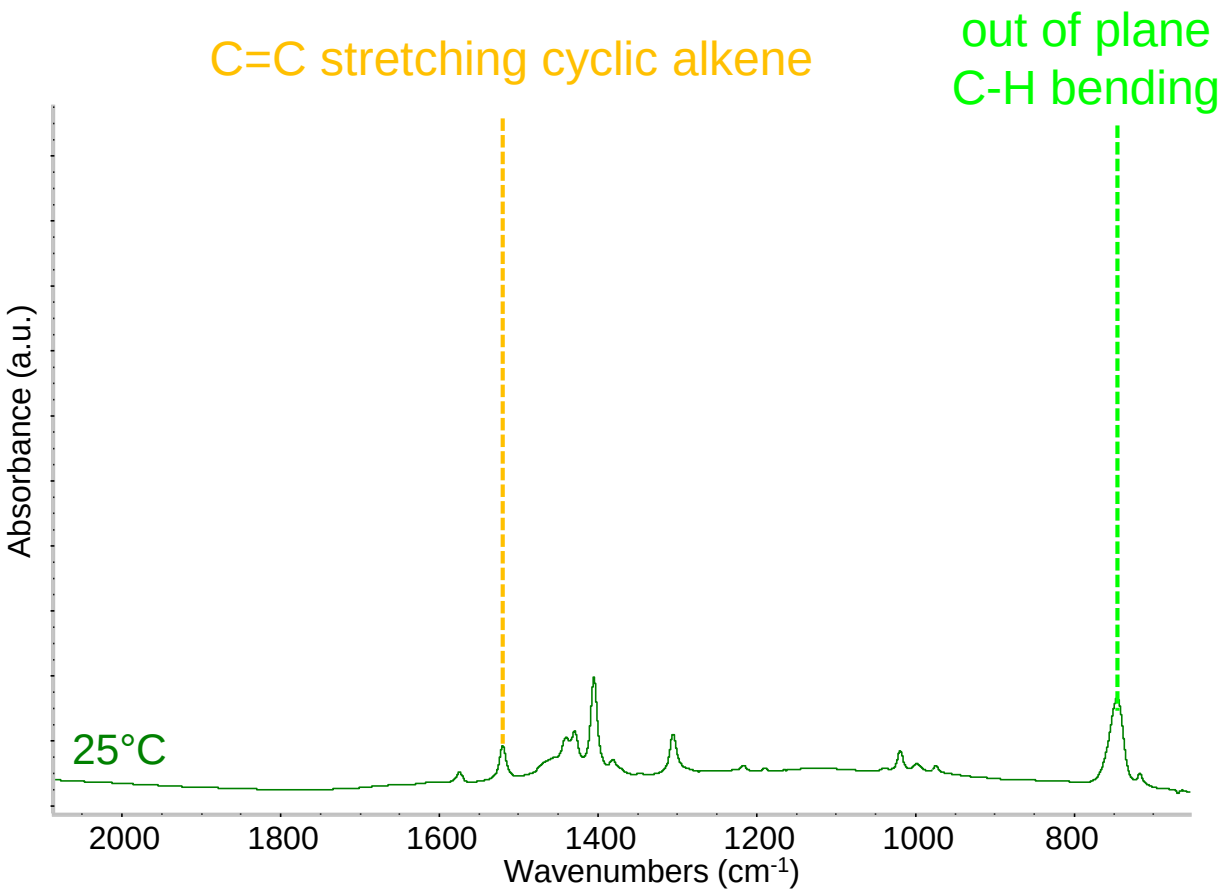
Mechanism of the functionalization reaction

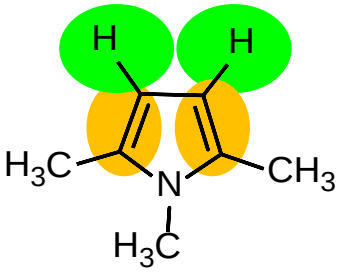
Investigation with a model compound



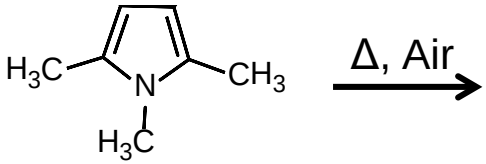
- ☞ Analysis of: liquids, HSAG/TMP adducts
- ☞ FT-IR and ^{1}H-NMR spectroscopies
- ☞ FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling.

1,2,5-Trimethylpyrrole (TMP)

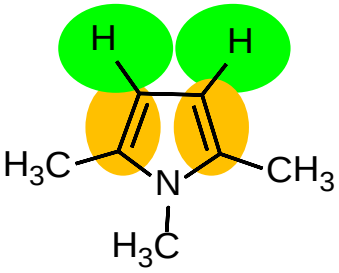


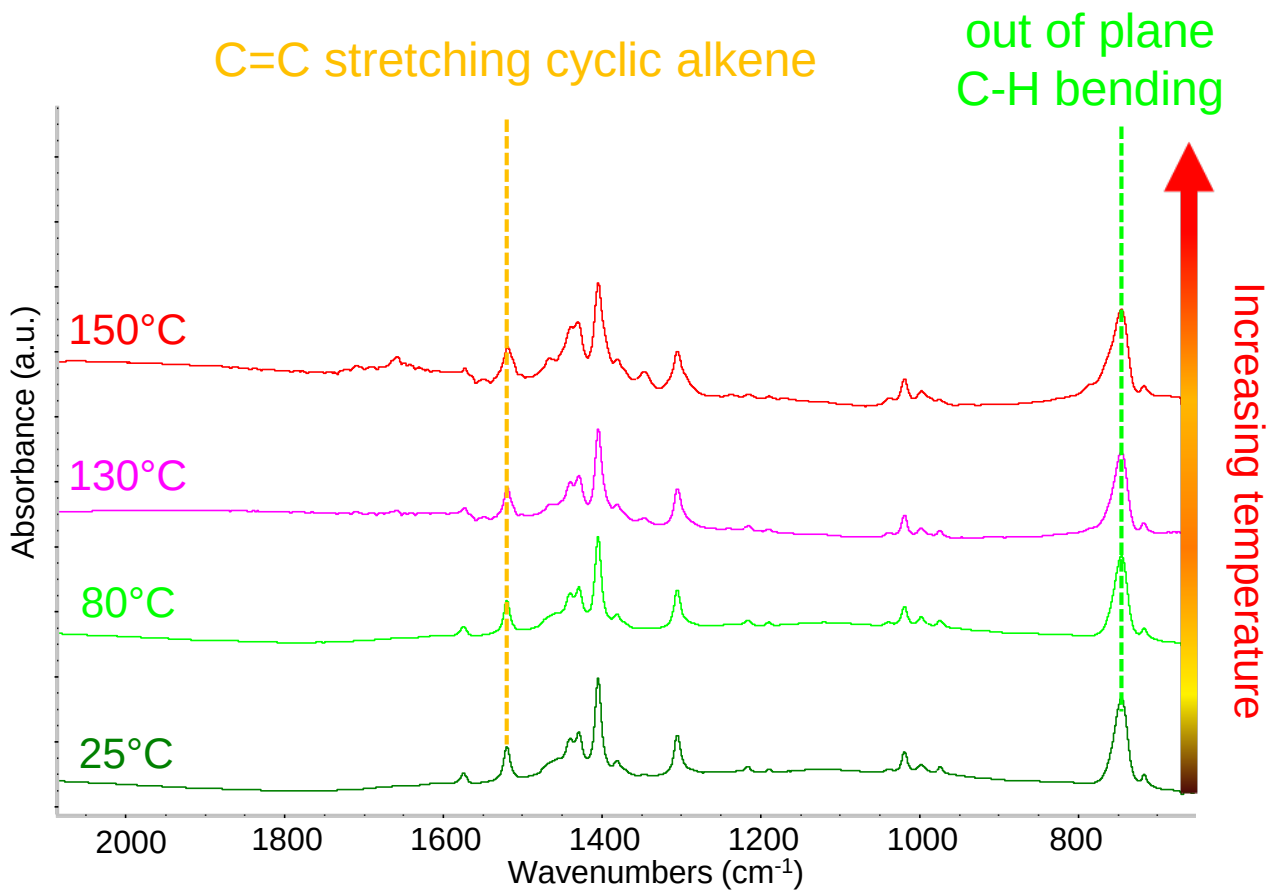


TMP + Air - From 25°C to 150°C

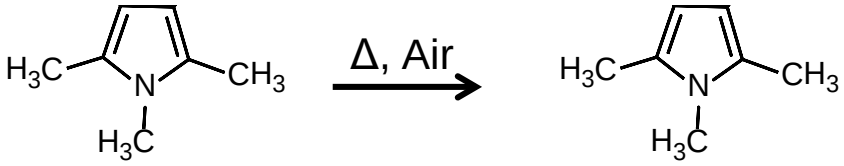


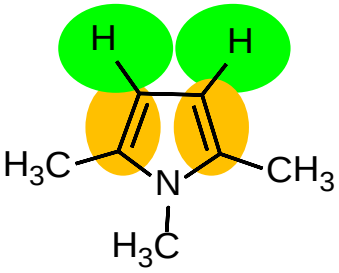
Δ, Air

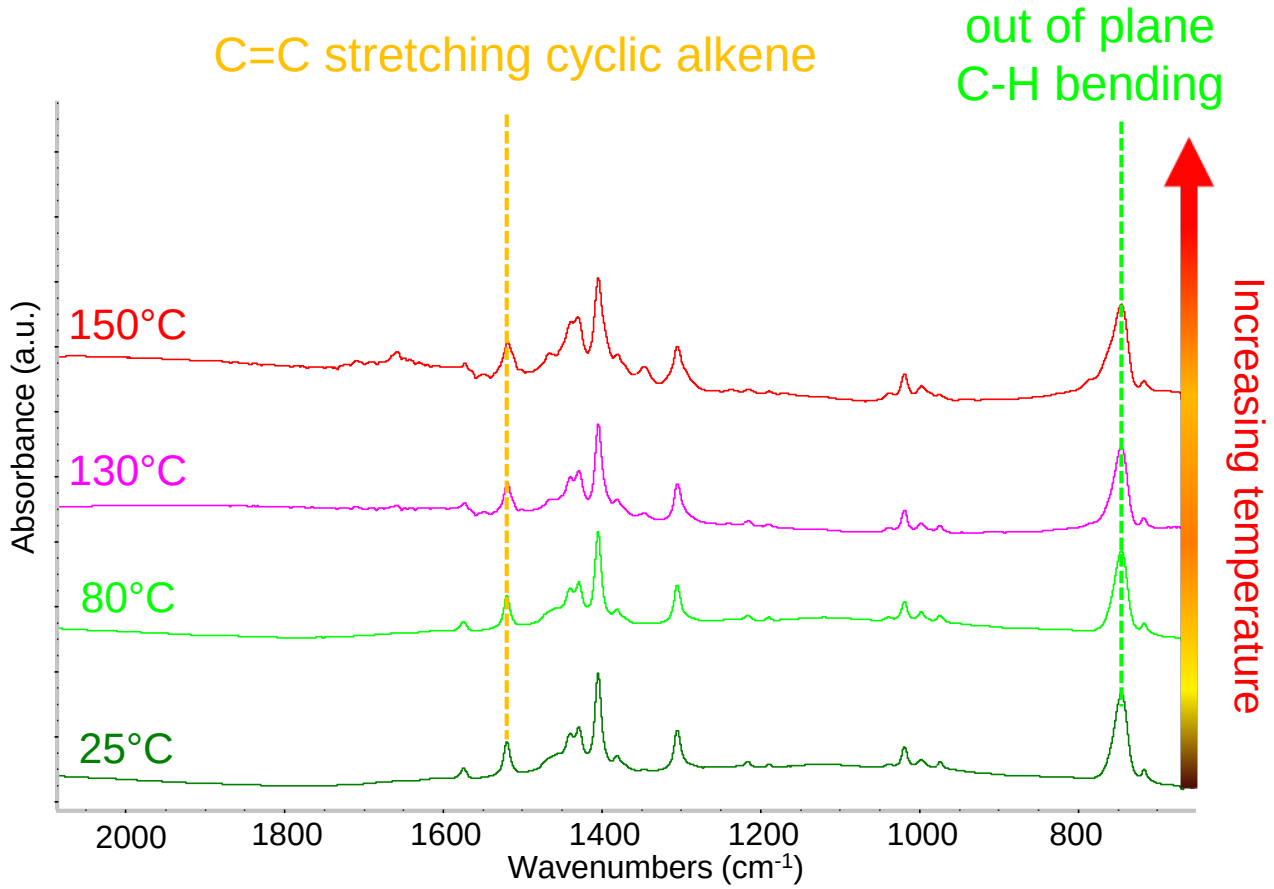




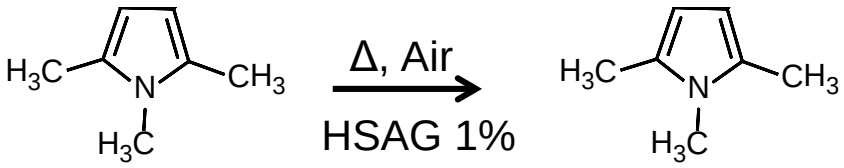
TMP + Air - From 25°C to 150°C

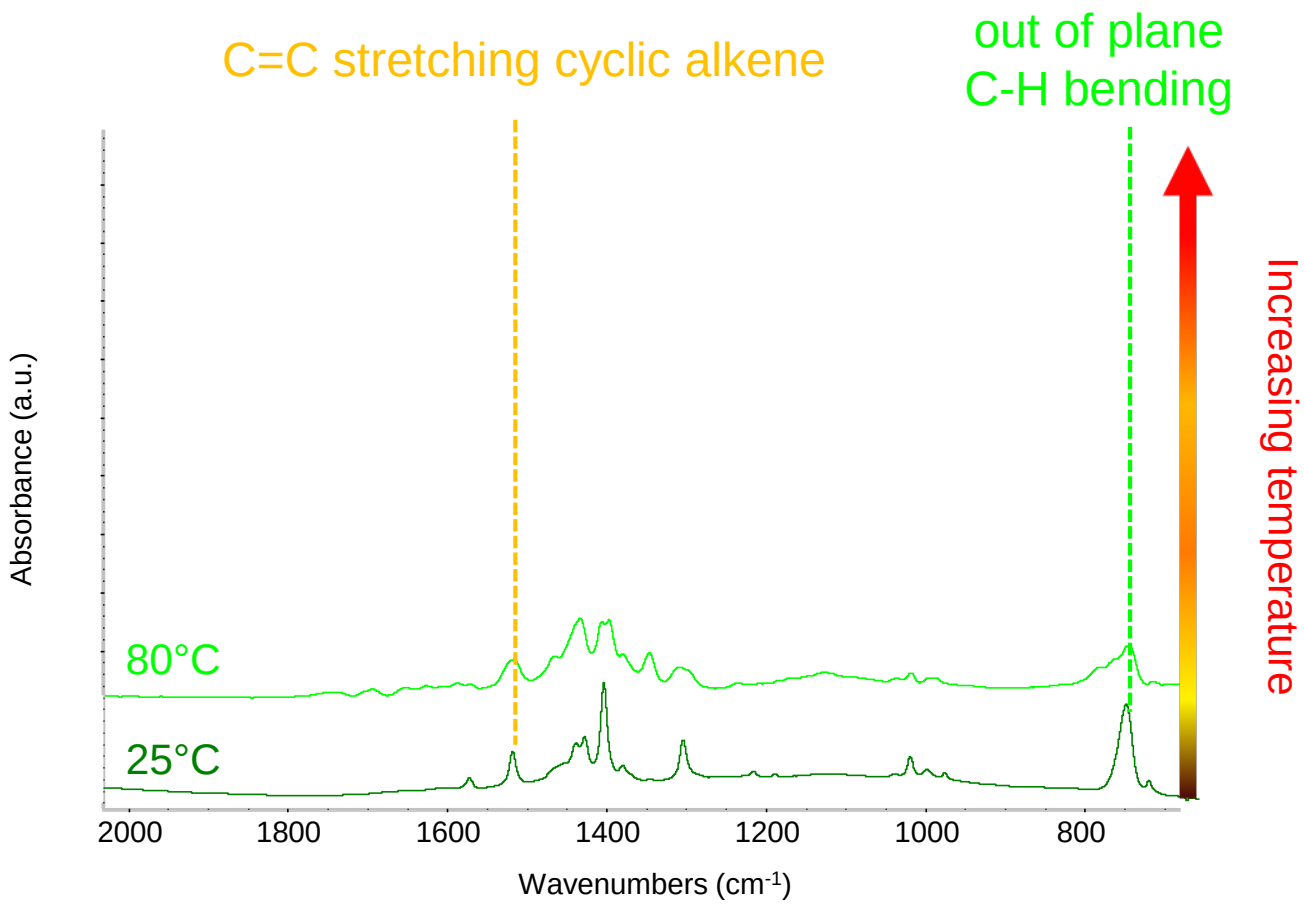


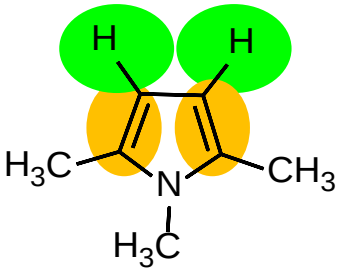




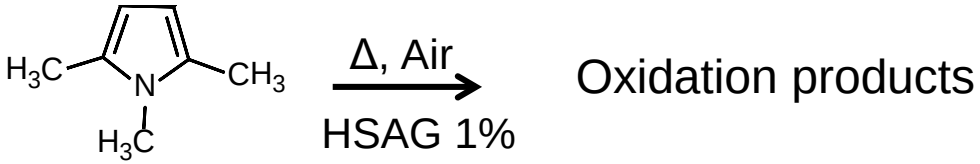
TMP + HSAG 1% / Air - From 25°C to 80°C

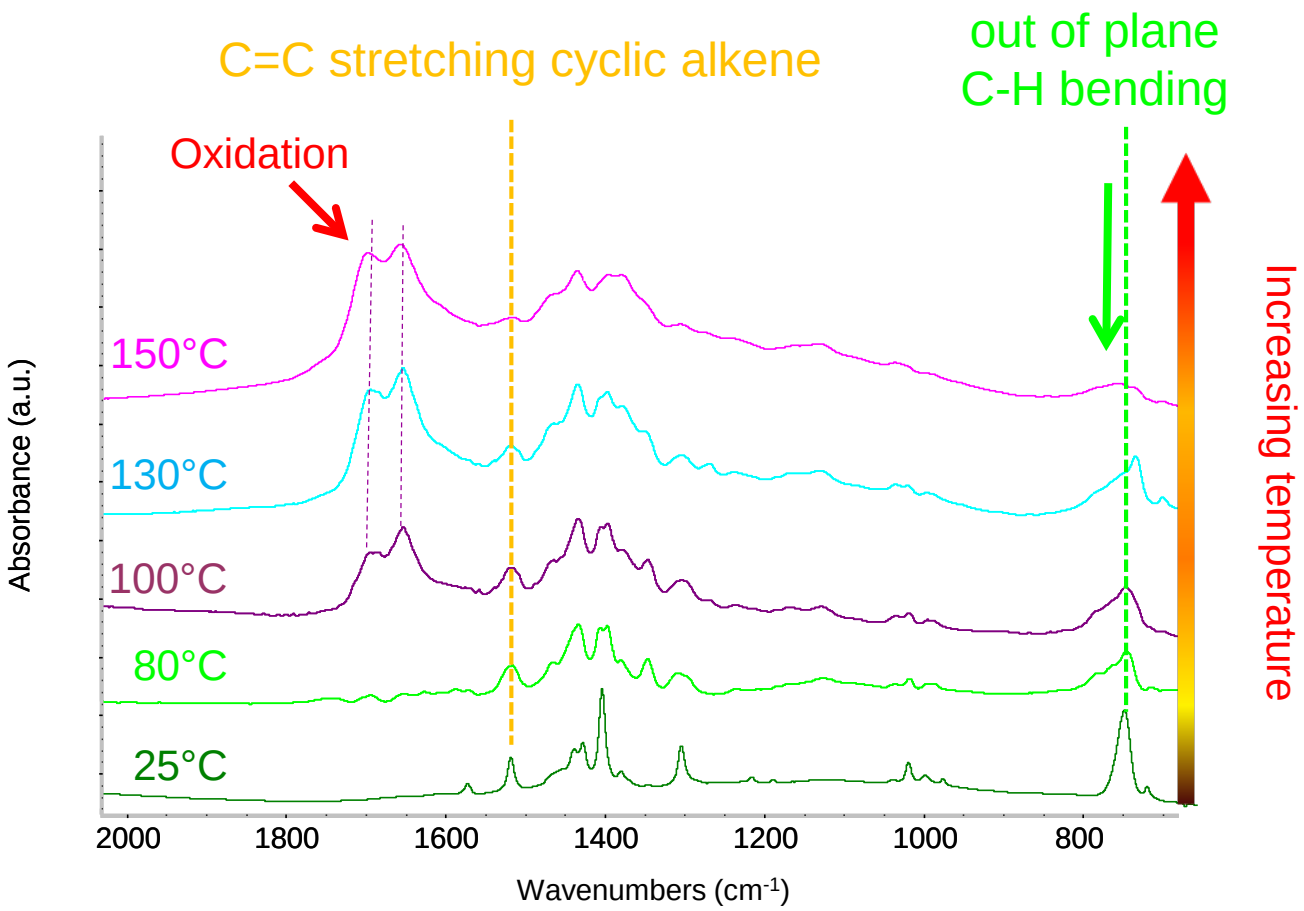


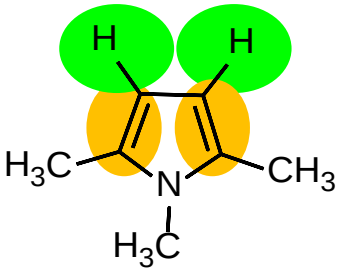




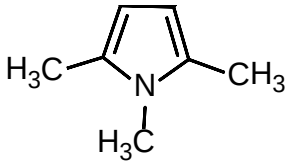
TMP + HSAG 1% - from 100°C to 150°C







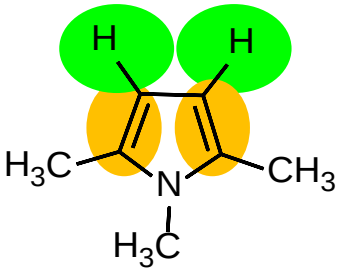
TMP + HSAG 1% - @ 150°C

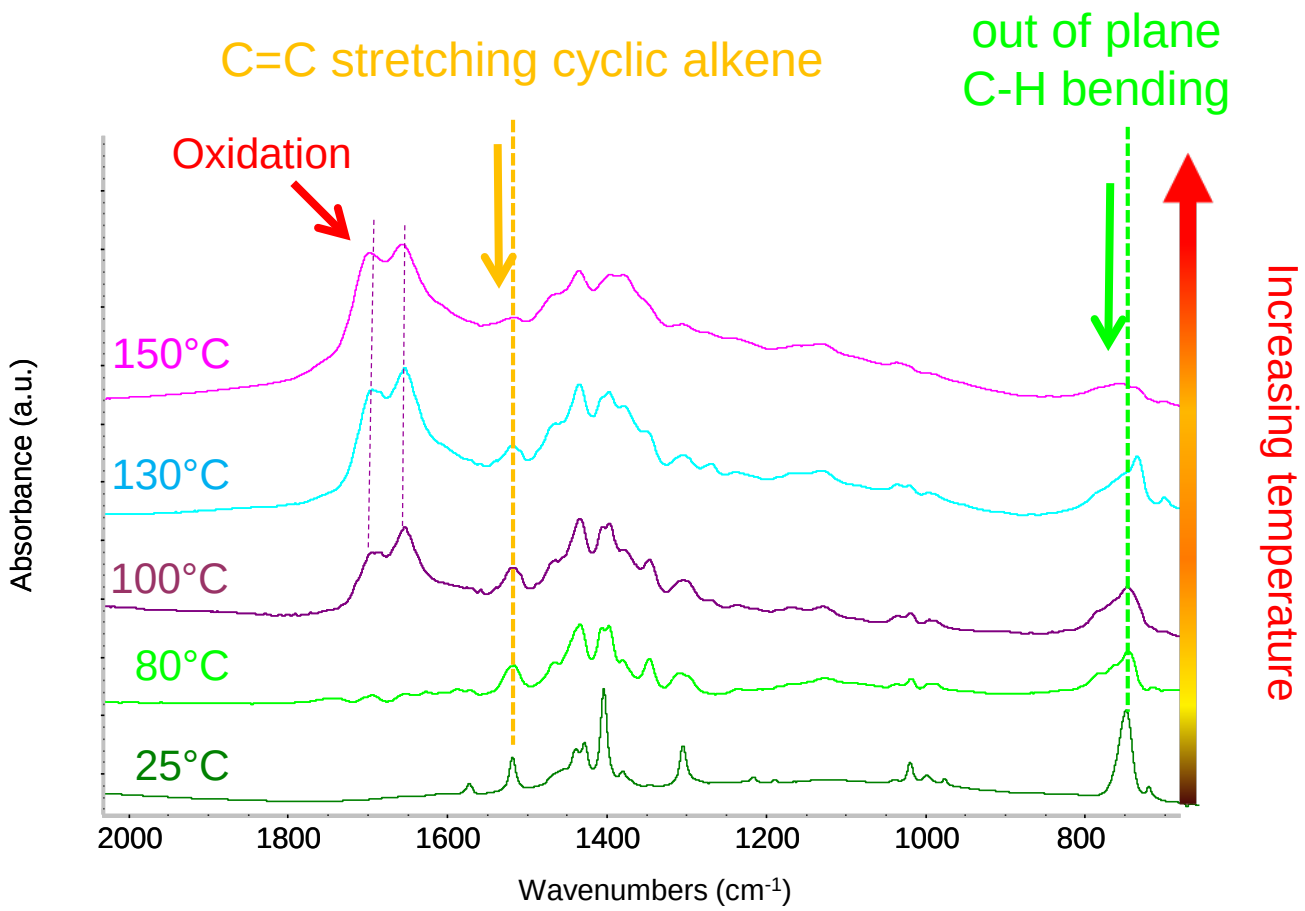


Δ, Air

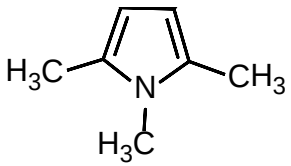
HSAG 1%

Reaction products of intra-annular double bonds





TMP + HSAG 1/1 - from 25 to 150°C



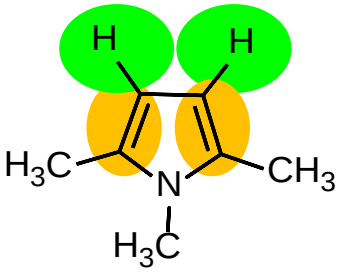
\+ HSAG

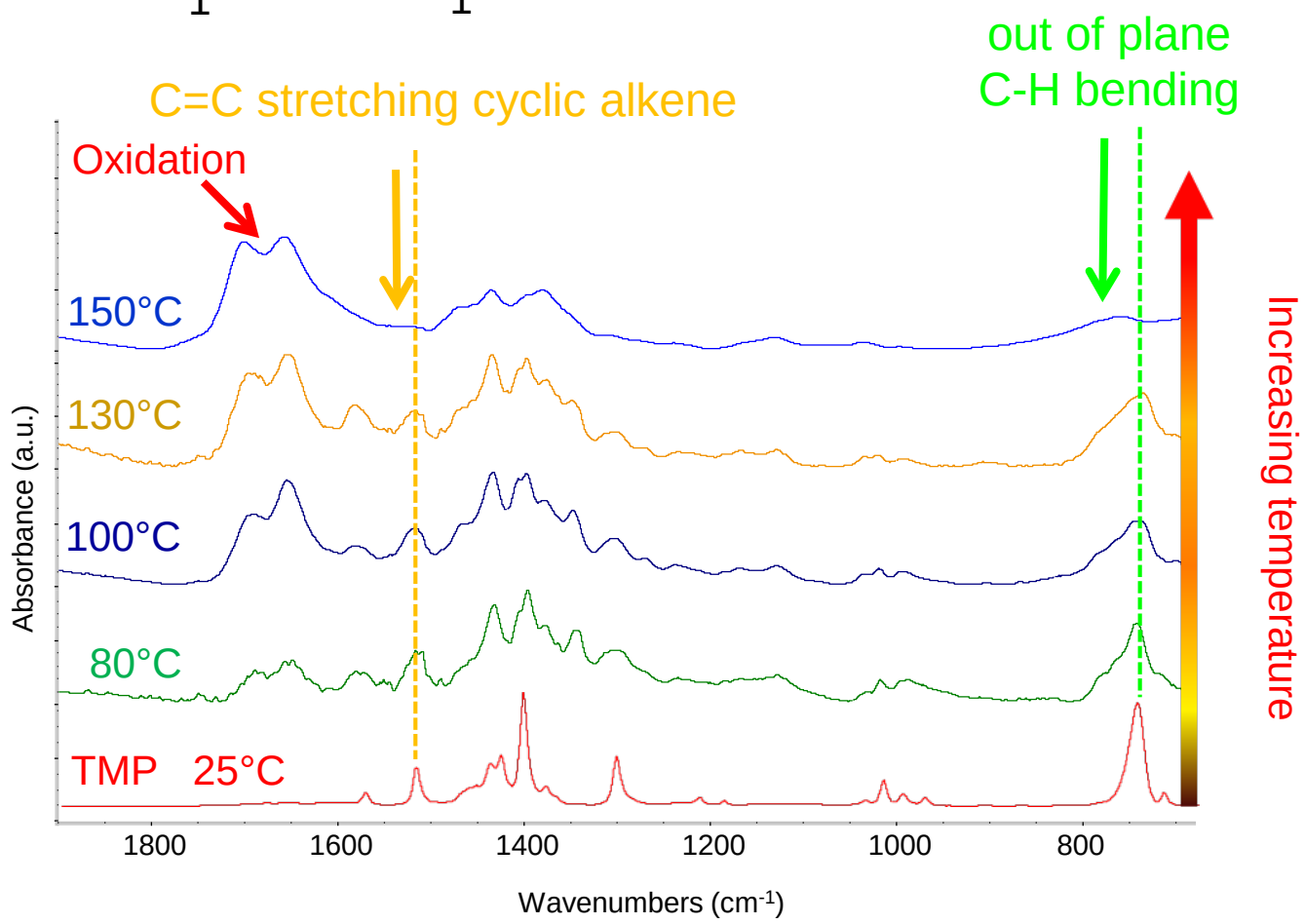
Δ, Air

Oxidation products

Reaction products of intra-annular double bonds

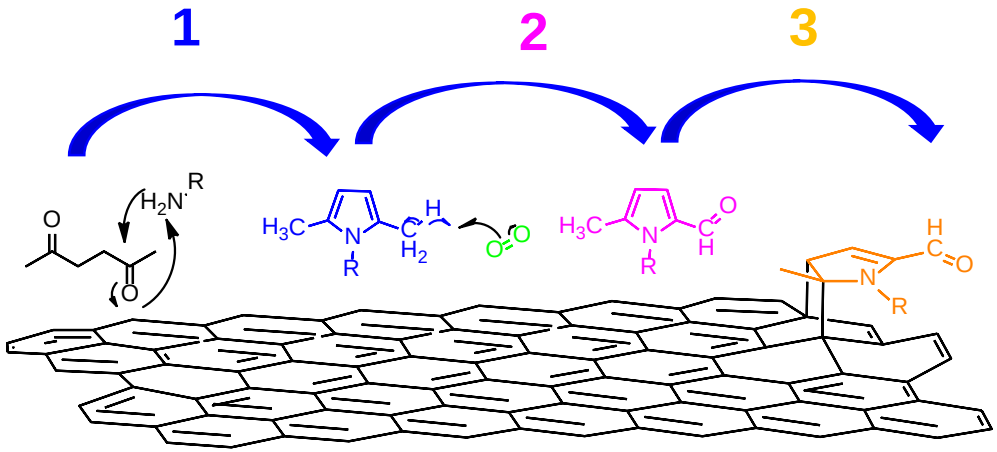
1 1





Facile functionalization of carbon materials

Hypothesis for the mechanism



Facile functionalization of carbon materials

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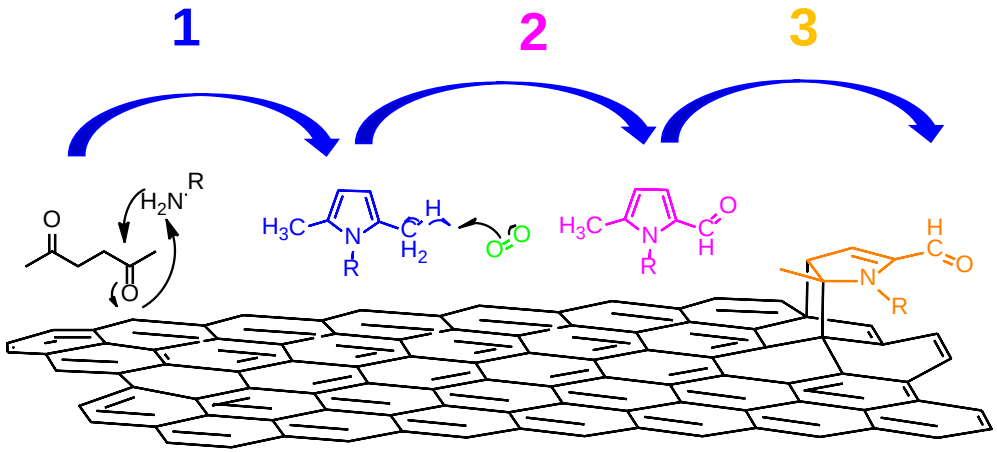
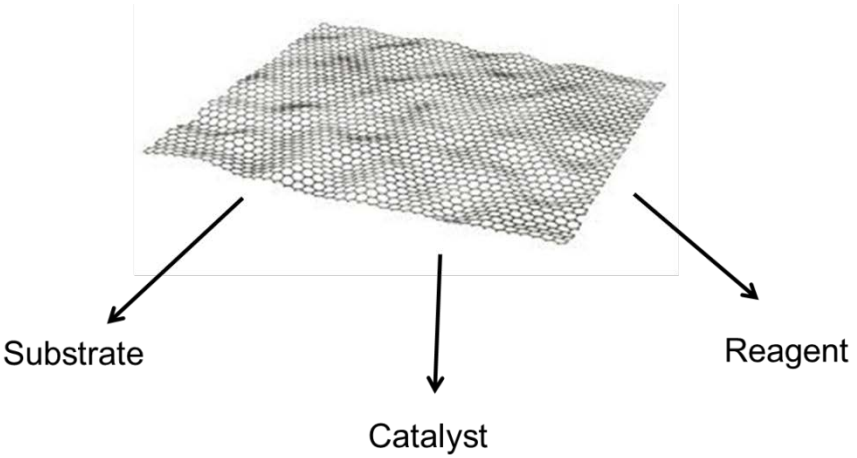
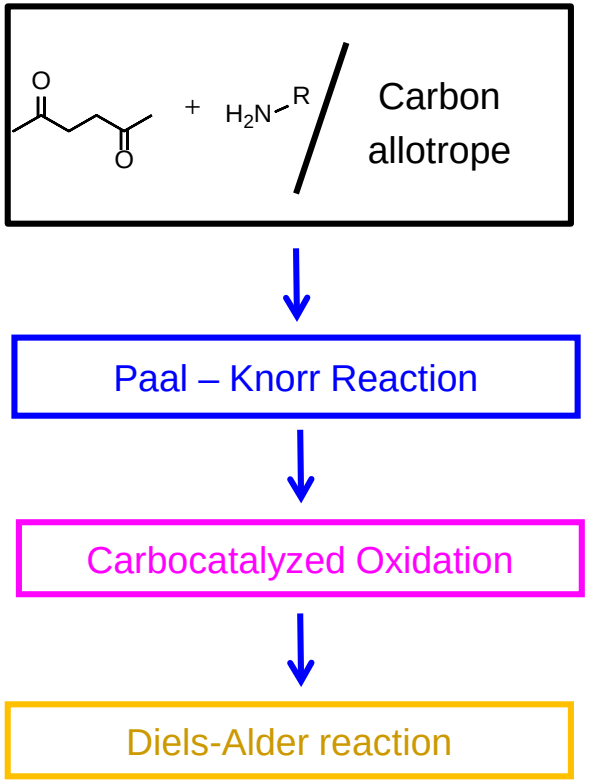
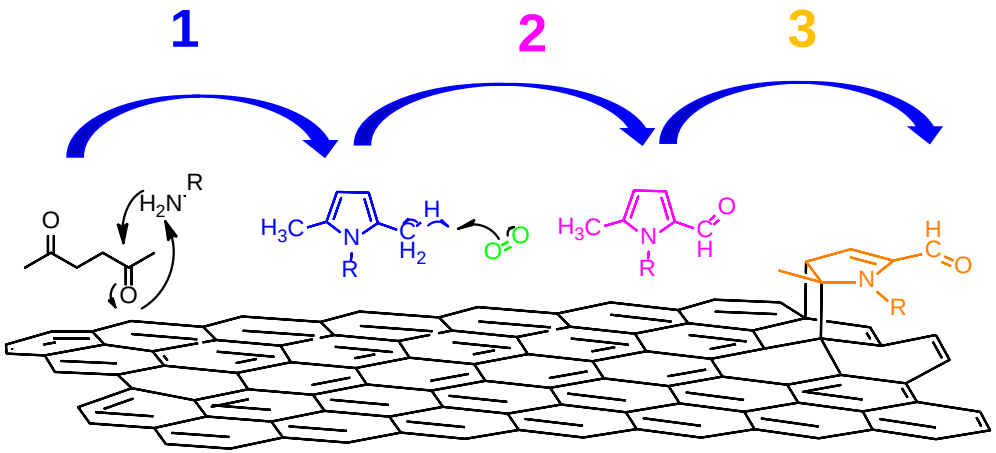




Facile functionalization of carbon materials

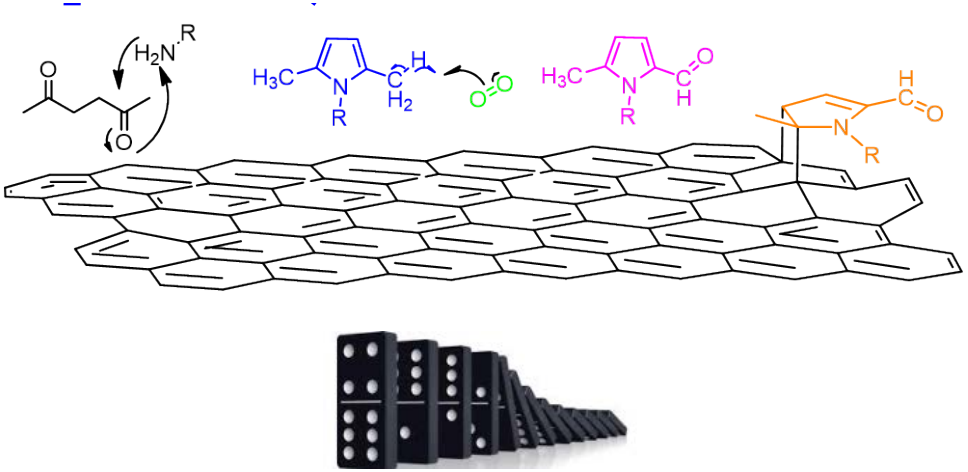
Hypothesis for the mechanism





Thanks to the carbon allotrope!

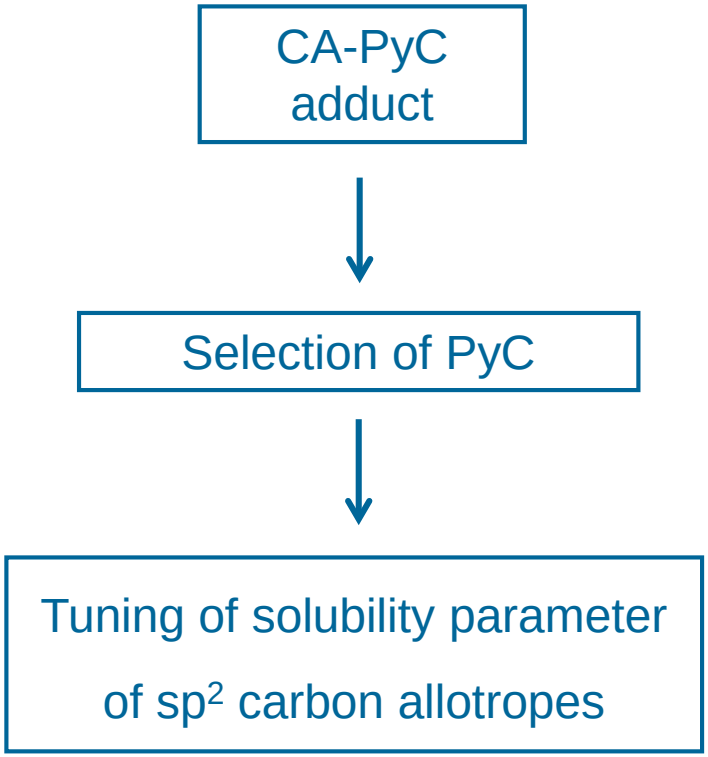
- Support: absorption of pyrrole ring thanks to π-π interaction
- Oxidation catalyst: protection of pyrrole ring and oxidation of lateral substituent
- Substrate for the cycloaddition reaction, i.e. for functionalization



Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., Bongiovanni, R. and Galimberti, M, 2019. Nanomaterials, 9(1), p.44.

Applications

Tuning of solubility parameter of sp^2 carbon allotropes (CA)



CA / PyC adducts - Tuning of solubility parameters

Experimental determination

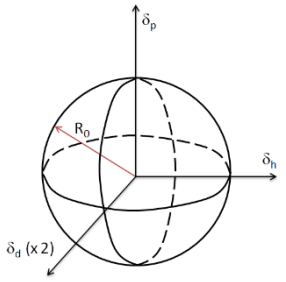
↓

Stable suspensions
in solvents
with different δ

Theoretical predictions

↓

Computational model:
Hansen solubility parameters



Evaluation of solubility parameters of HSAG-PyC - Experiments

Adduct HSAG-	solvents water	isopropanol	ethyl acetate	toluene	heptane
TMP	bad (↓)	good	good	good	good
EP	bad (↑)	bad (↓)	good	bad (↓)	good
DDcP	bad (↑)	good	good	bad (↓)	bad (↓)
APTESP	bad (↑)	bad (↓)	bad (↓)	good	good
Gly	bad (↓)	good	good	good	bad (↓)
SP	good	good	good	bad (↓)	bad (↓)

No suspension: **bad**

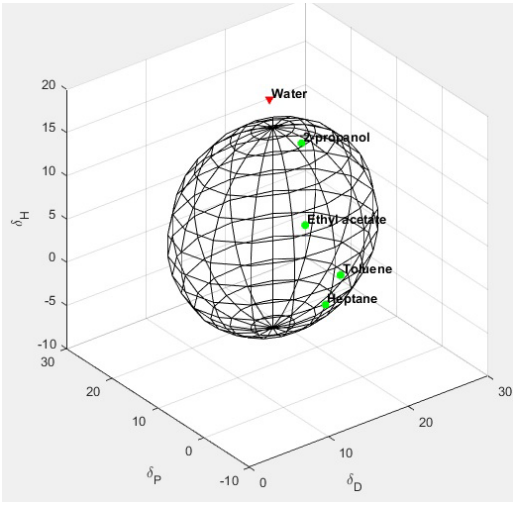
Unstable suspension: **bad**

Stable suspension: **good**

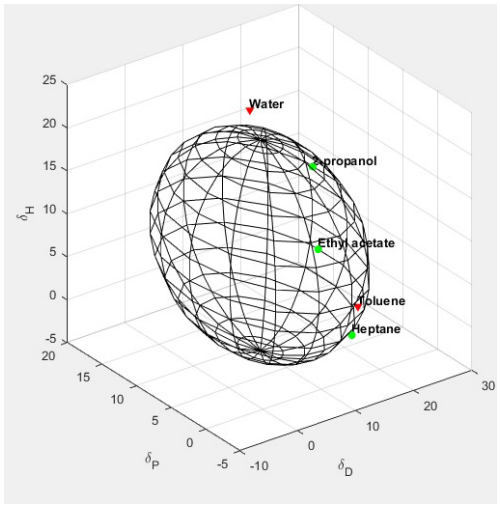
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

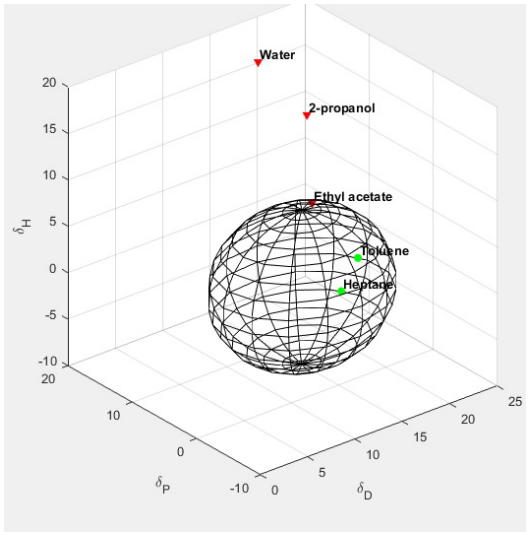
HSAG-TMP



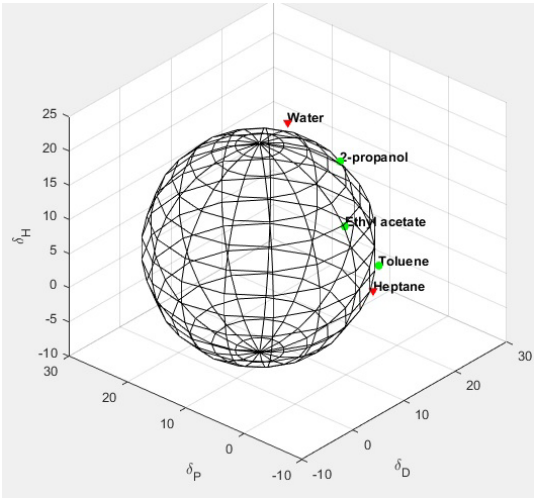
HSAG-DDcP



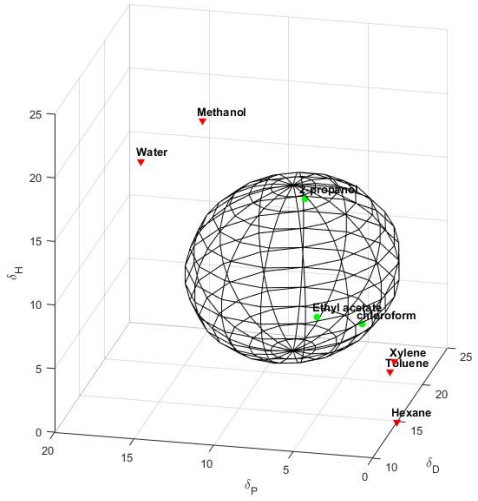
HSAG-APTESP

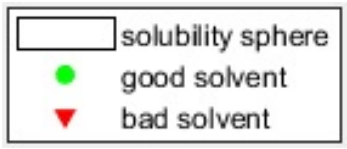


HSAG-GlyP



HSAG-SP



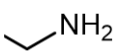


V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

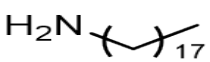
Evaluation of solubility parameters of HSAG-PyC - δ values

Sample	δ_D	δ_P	δ_H	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-TMP	14.6	10.3	5.6	11.6
HSAG-DDcP	8.5	7.5	8.3	12.3
HSAG-APTESP	12.7	2.3	0.5	8.3
HSAG-SP	12.8	2.0	8.9	13.8
HSAG-GlyP	6.9	12.1	5.3	15.3

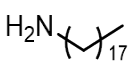
Amount of PyC on HSAG: about 5% mol



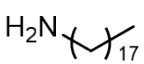
TMP



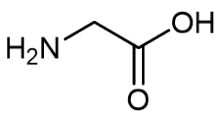
EP



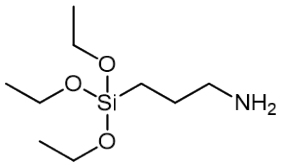
DDcP



ODcP



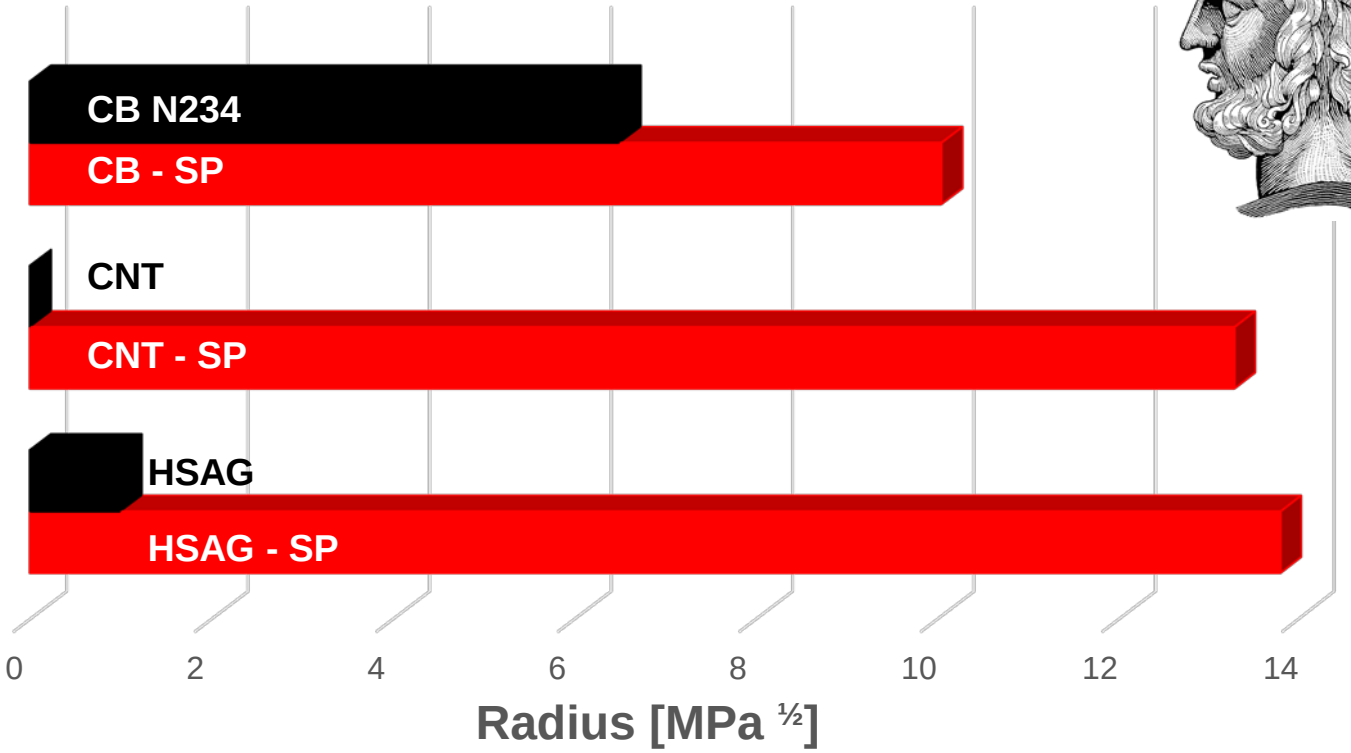
GlyP



APTESP

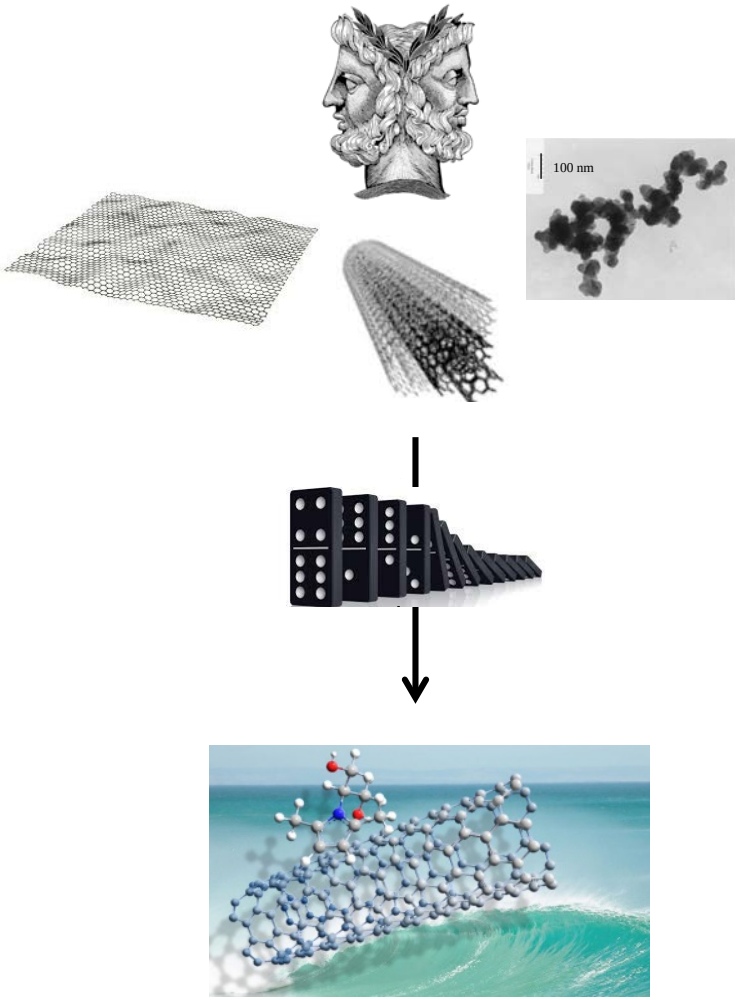
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of CA-SP - Radius comparison



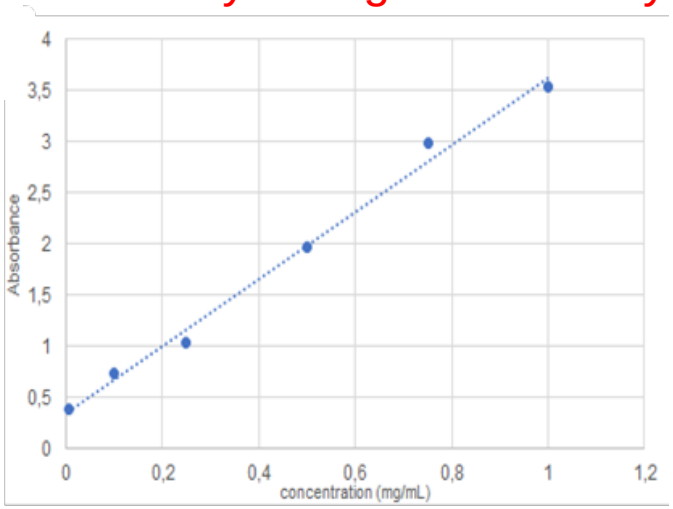
(*) Amount of SP on CA: 10 mass%

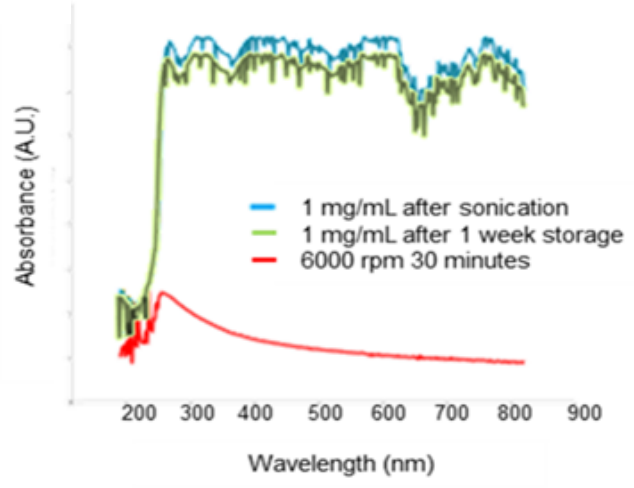
Applications of functionalized sp^2 carbon allotropes

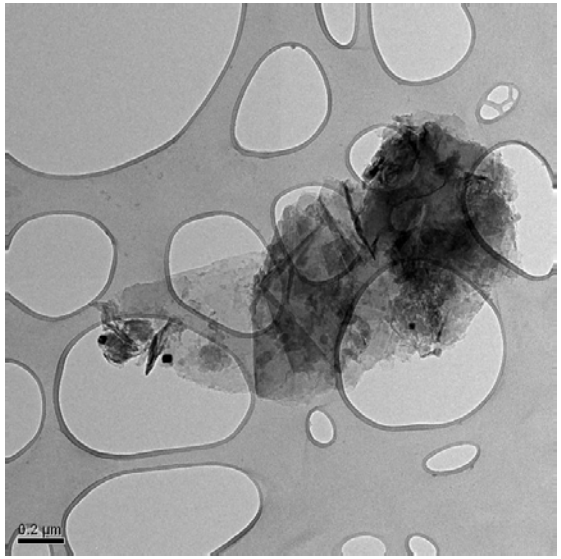


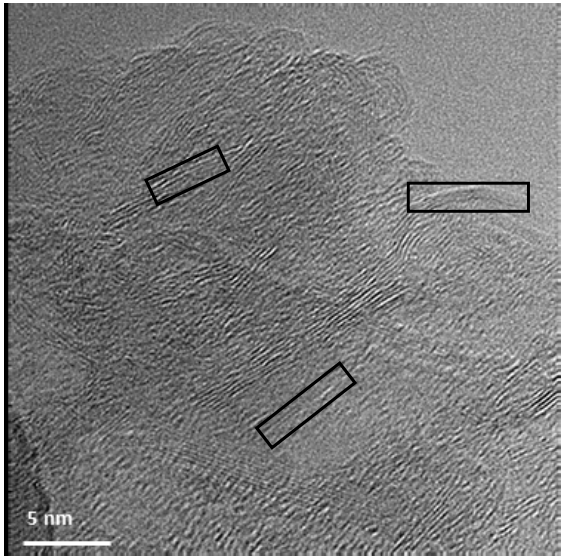
Ultimate dispersions in water of few layers graphene

By tuning the solubility parameter of graphene layers



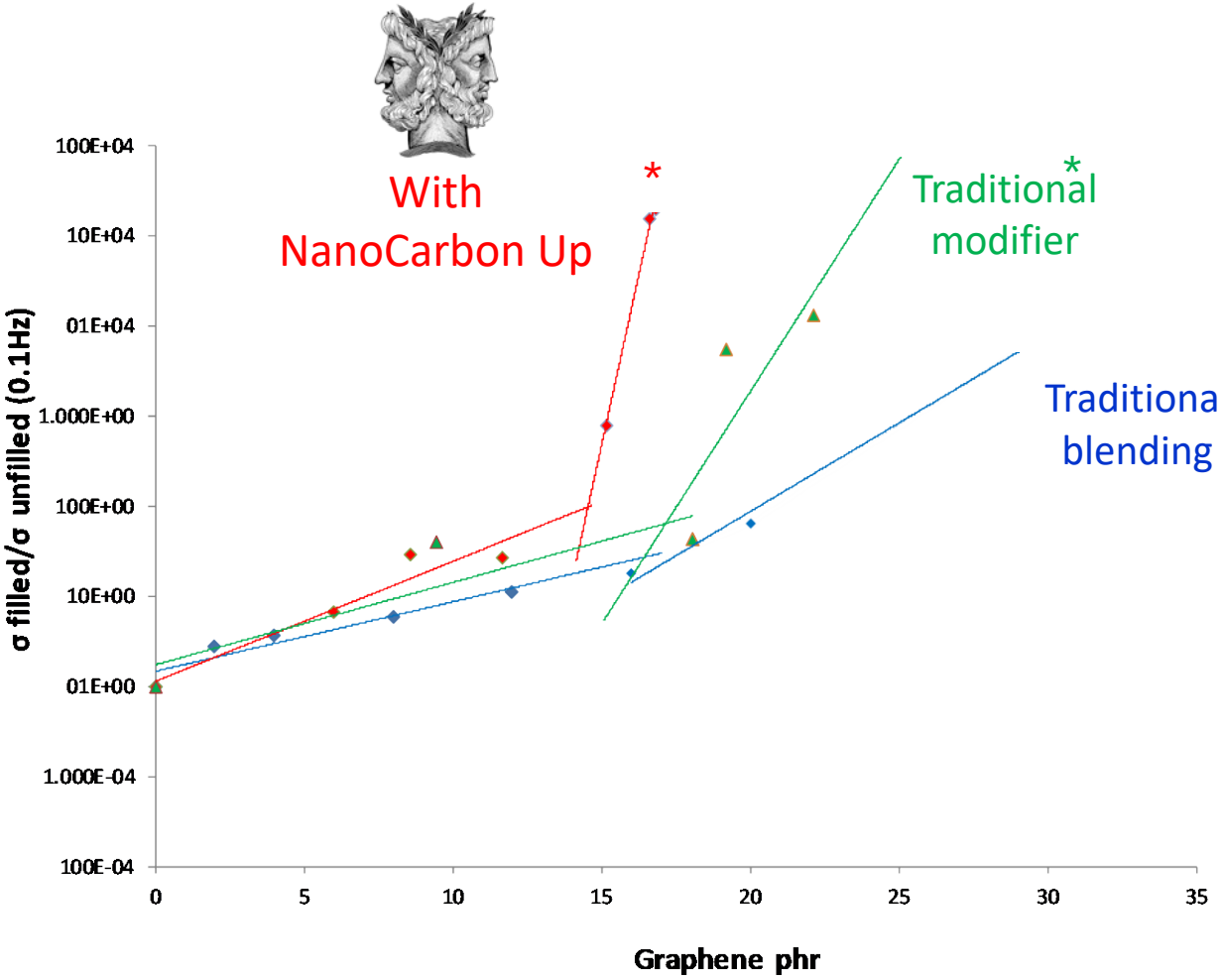






2-3 stacked layers

Graphene based polymer composites



Polymer = NR

* From NR latex dispersion

☞ Better electrical conductivity

CB-SP in CB/Silica based composite

Recipes

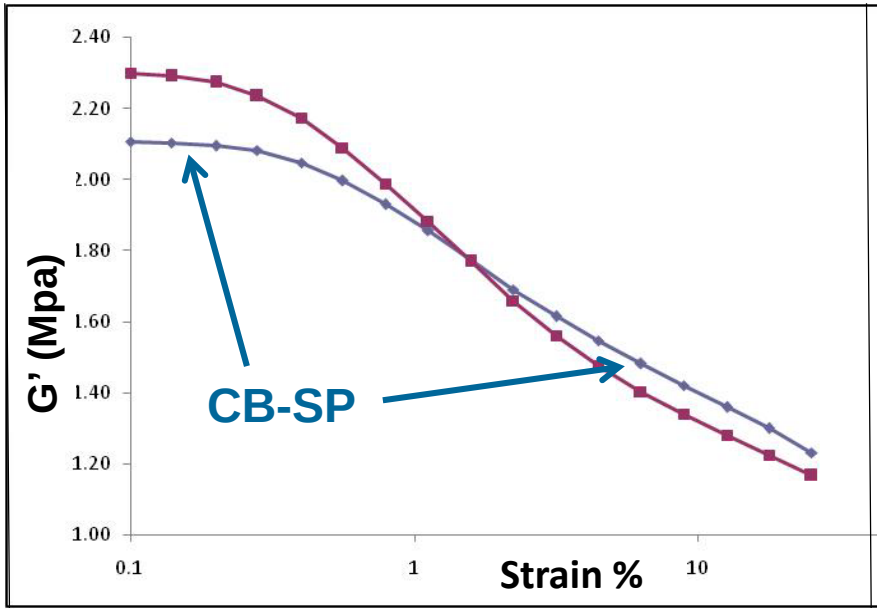
Ingredient	With CB	With CB-SP
IR	50	50
BR	50	50
Silica	25	25
CB N326	25	0
CB N326-SP	0	27
CB N326	0	25
SP	0	2

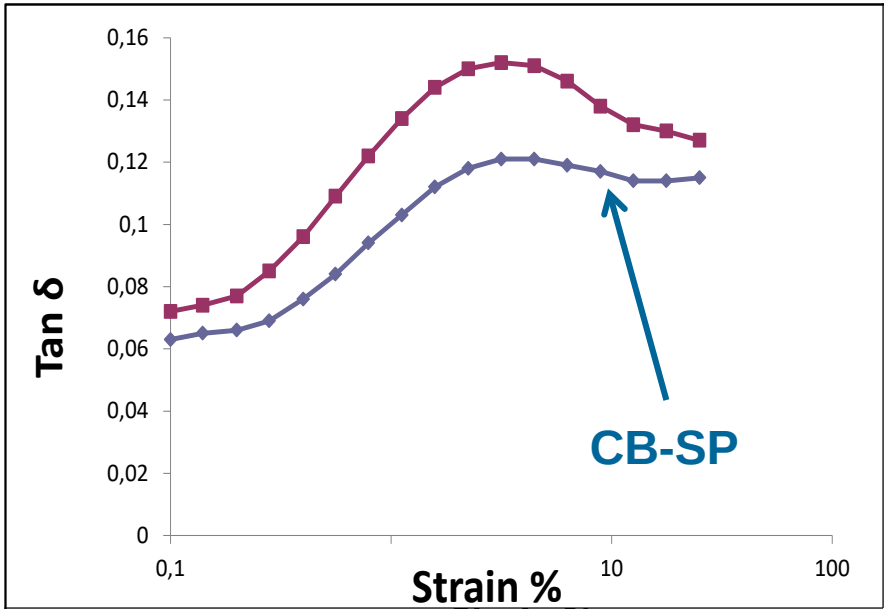
Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,

Sulphur 1.5, TBBS 1.8

Galimberti, M., Barbera, V., Sebastiano, R., Citterio, A., Leonardi, G., Valerio, A.M., WO 2016 050887 A1

Dynamic-mechanical properties





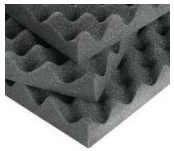
With CB-SP

- ☞ Lower Payne Effect and crossover of the curves
- ☞ Lower Tan delta

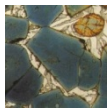
Galimberti, M., Barbera, V., Sebastiano, R., Citterio, A., Leonardi, G., Valerio, A.M., WO 2016 050887 A1

Conclusions





- 10 families of patents
- Networking
- JDA & Licensing
- Pilot plant production
- Education and training: PhD, Master thesis, secondments

ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

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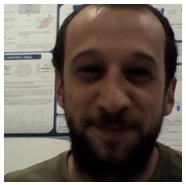

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Thanks for the attention!