Edge functionalization of graphene layers with biobased molecules

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Global virtual summit on Carbon, Graphene, 0D, 1D, and 2D Materials
July 22-23, 2021

Items of the presentation

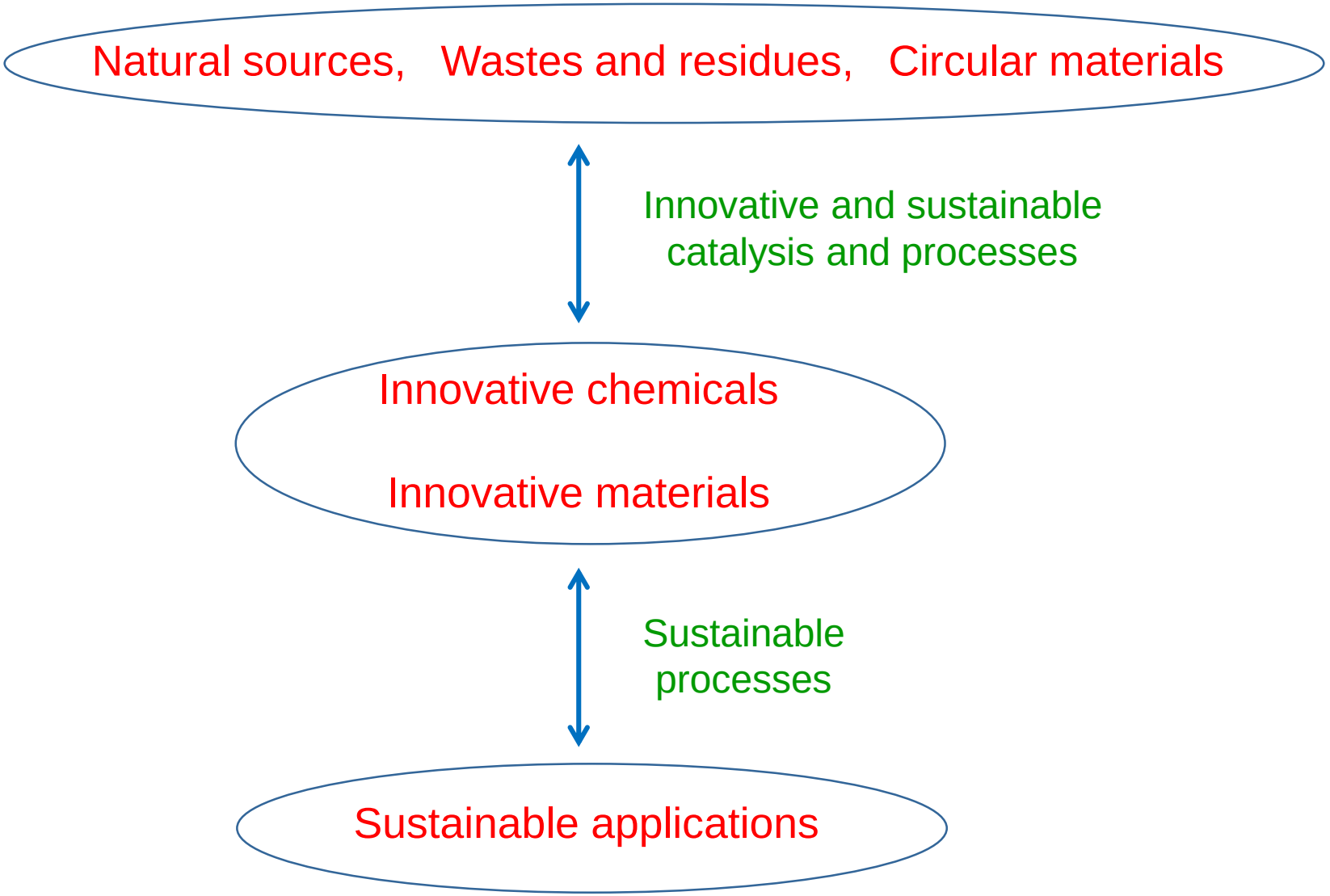
- Sustainability for innovation
- Biosourced C-3 and C-6 building blocks
- Pyrrole compounds and pyrones
  for the edge functionalization of graphene layers
- Edge functionalized graphene layers:
  properties and applications
- Production of few layer graphene and applications

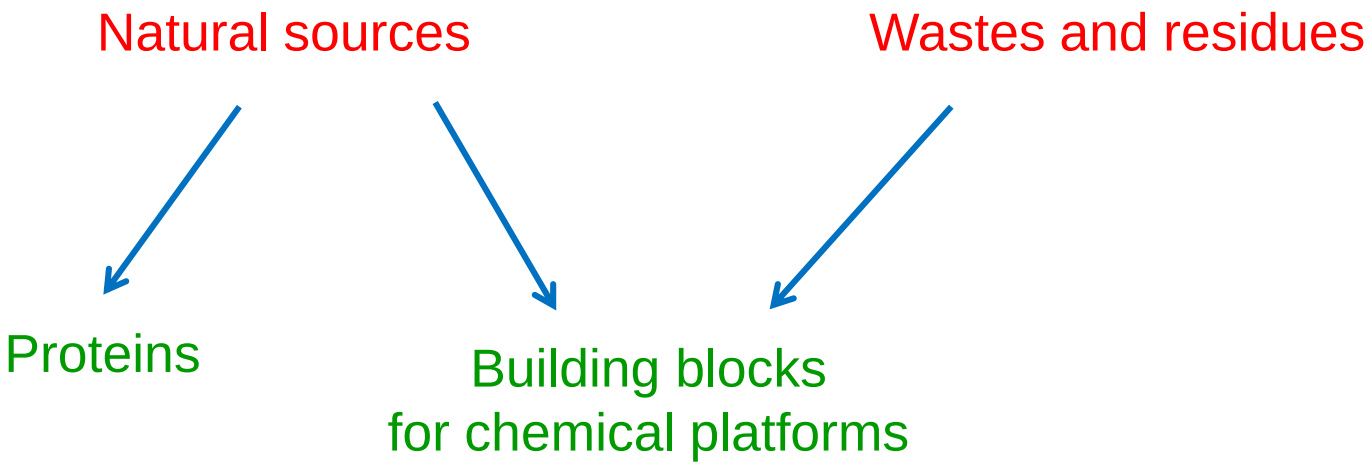
ISCaMaP

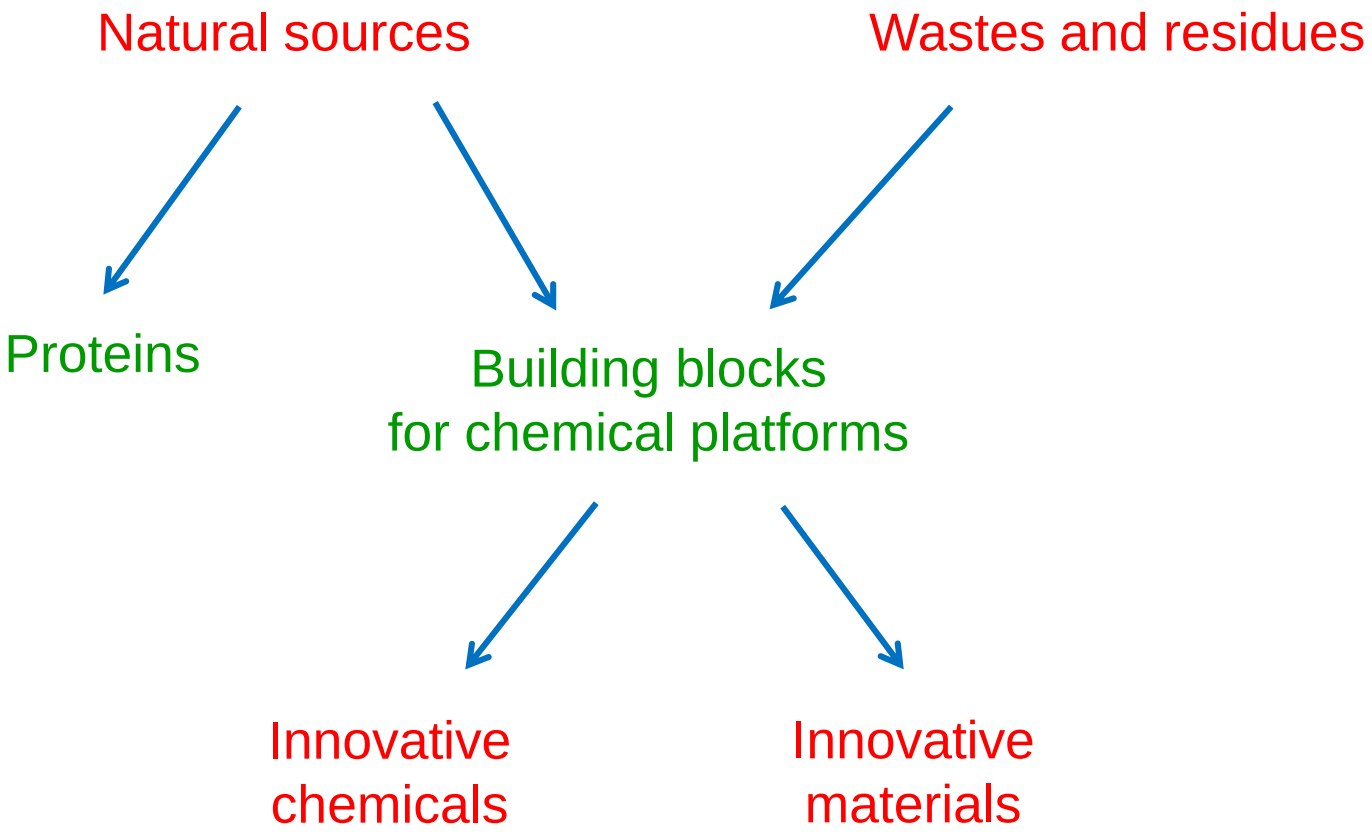
Innovative Sustainable Chemistry and Materials and Proteomics Group

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

ISCaMaP Strategy: sustainability for innovation




Natural sources
Wastes and residues
Proteins
Building blocks
for chemical platforms


Natural sources
Wastes and residues
Proteins
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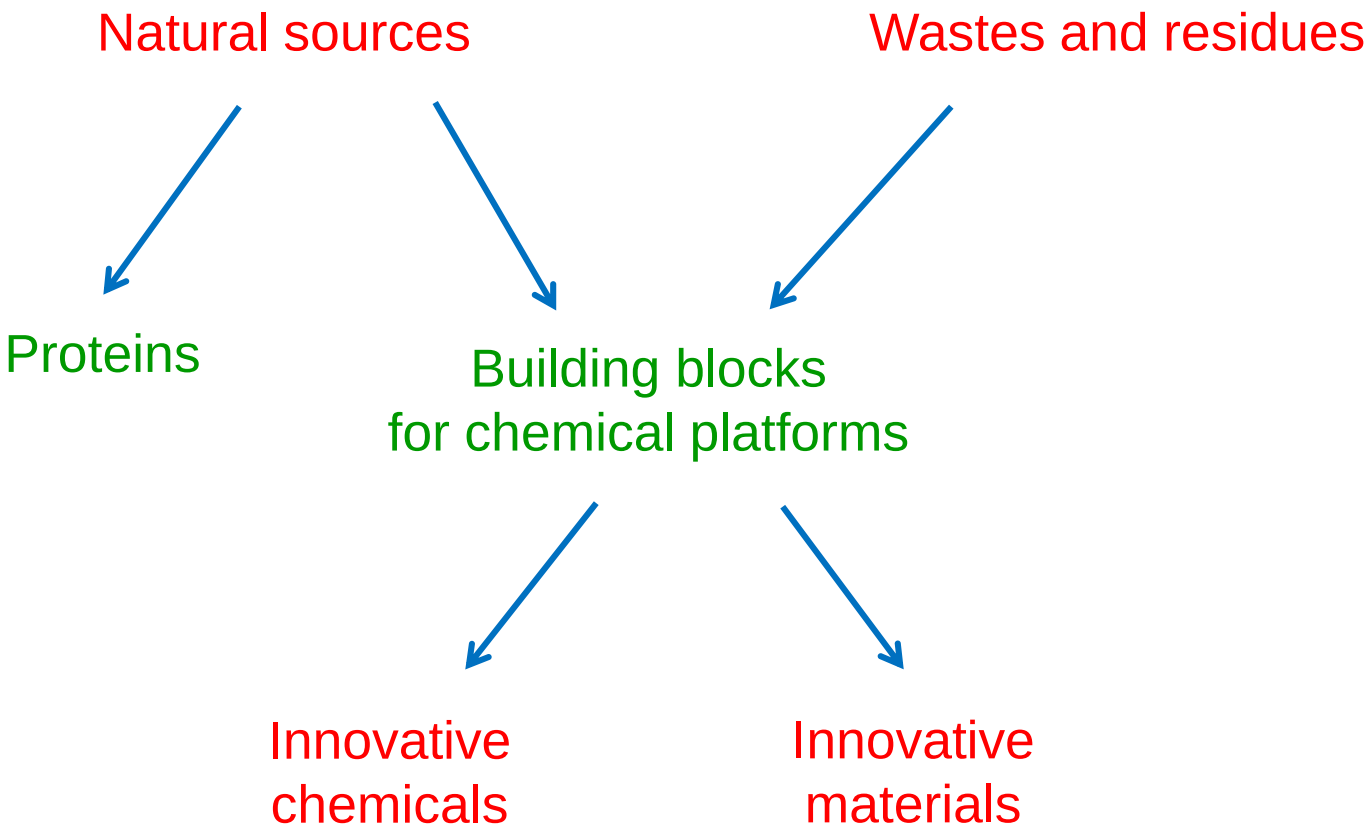
Innovative
chemicals
Innovative
materials



☞ Chemicals, Additives, Modifiers, Polymers

The DOE's Top Chemical Opportunities

Four Carbon 1,4-Diacids: Succinic, Fumaric and Malic

2,5-Furan dicarboxylic acid

3-Hydroxypropionic acid

Glucaric acid

Glycerol

Aspartic acid

Itaconic acid

3-Hydroxybutyrolactone

Sorbitol (Alcohol Sugar of Glucose)

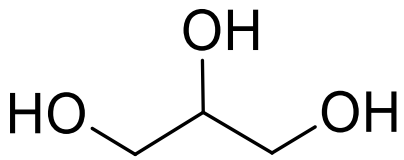
Xylitol/arabinitol (Sugar alcohols from xylose and arabinose)

Glutamic acid

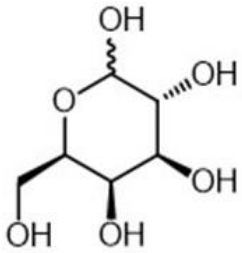
Levulinic acid

DOE = US Department of Energy

Innovative materials from C3 and C6 building blocks

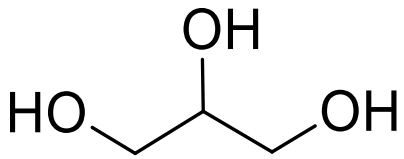


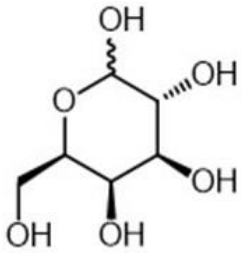
Glycerol, Sugars



Innovative materials from C3 and C6 building blocks

Glycerol, Sugars



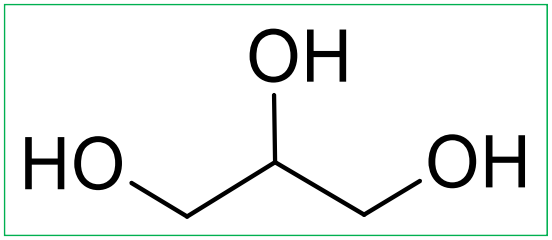


Biousourced substances + “Traditional Chemistry”

Innovative building blocks

C3 building blocks

Glycerol as the C3 building block



Propane-1,2,3-triol

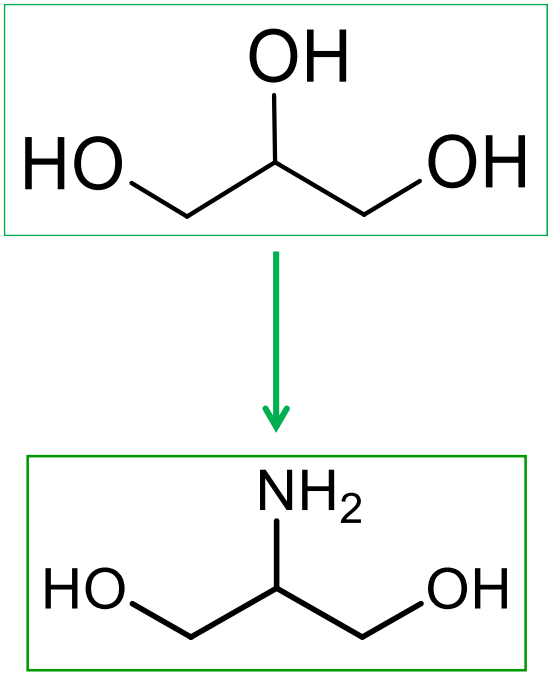
easily available, cheap raw material

main by-product of bio-diesel production

not toxic

biodegradable

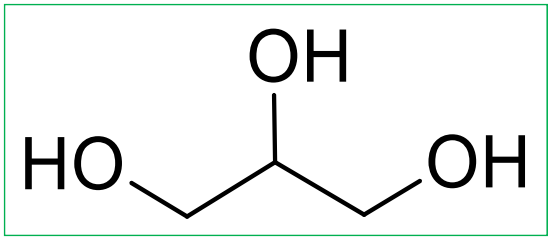
Glycerol as the C3 building block. From glycerol to serinol



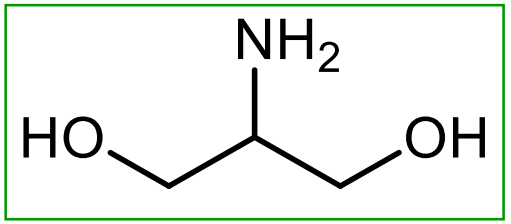
Propane-1,2,3-triol

2-Amino-1,3-propanediol

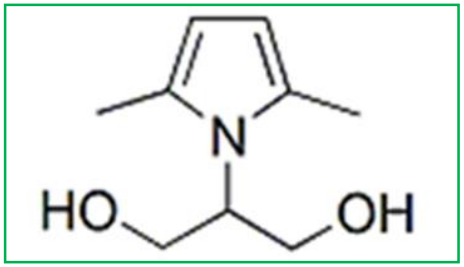
Glycerol as the C3 building block. From glycerol to serinol to serinol pyrrole



Propane-1,2,3-triol

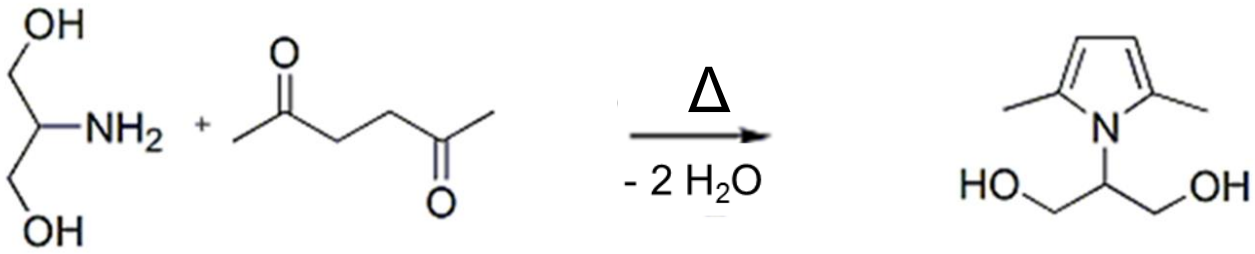


2-Amino-1,3-propanediol



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

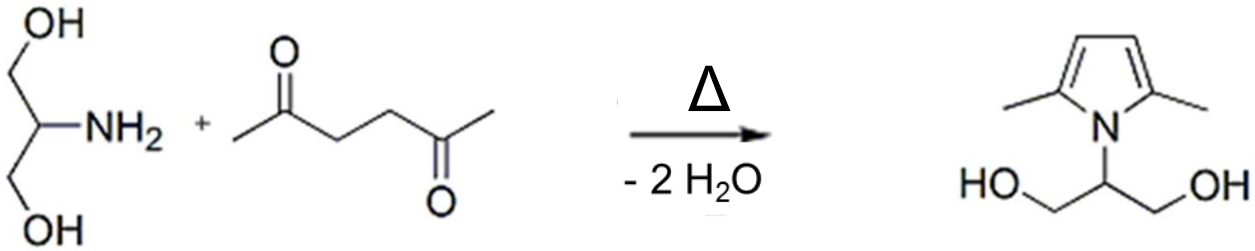
From serinol to serinol pyrrole

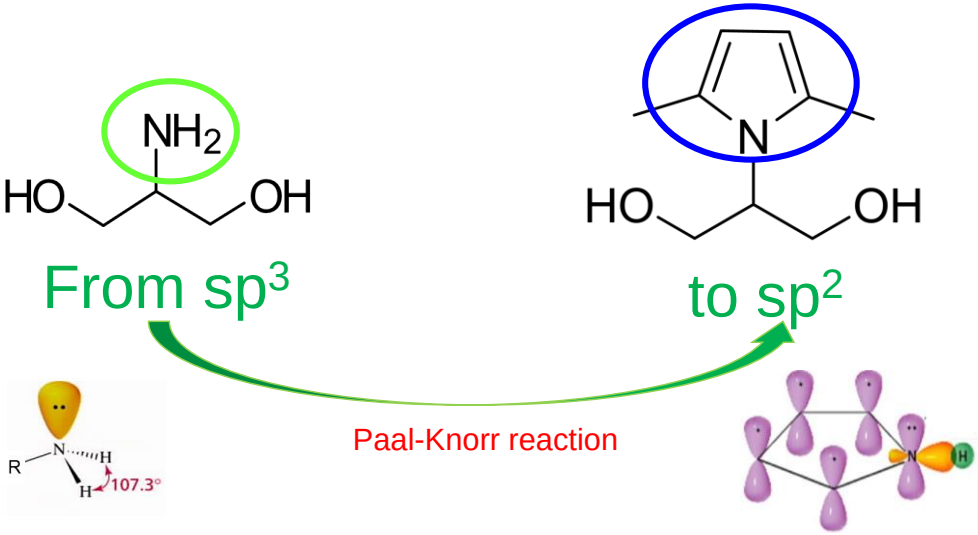


- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

US10329253 B2; EP3154939 B1. V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S. U. Shisodia, A. M. Valerio

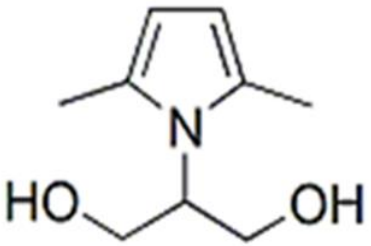
From serinol to serinol pyrrole





US10329253 B2; EP3154939 B1. V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S. U. Shisodia, A. M. Valerio

Serinol pyrrole as a biosourced *Janus* molecule

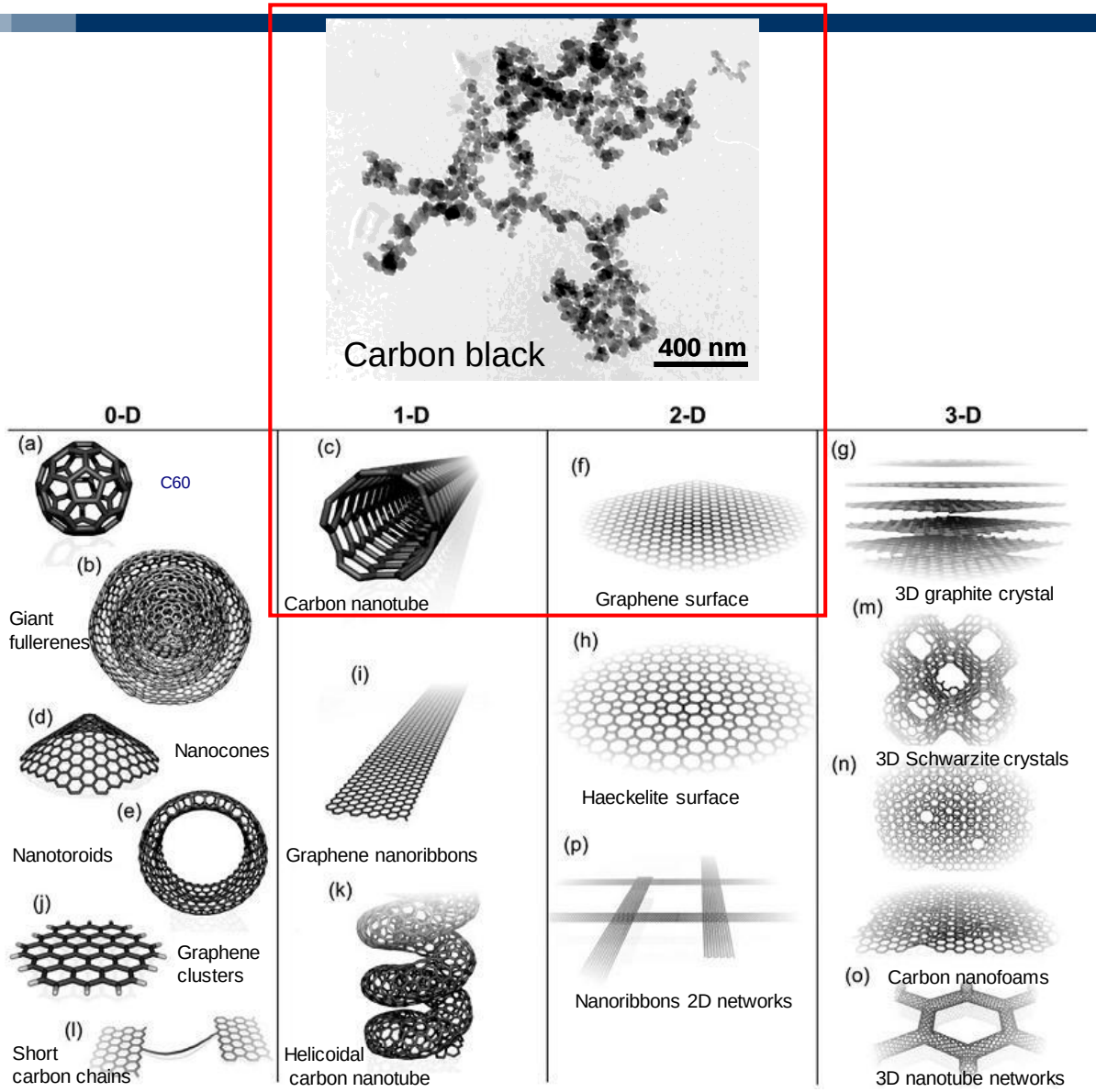


2-(2,5-dimethyl-1*H*-pyrrol-1-yl) -1,3-propanediol

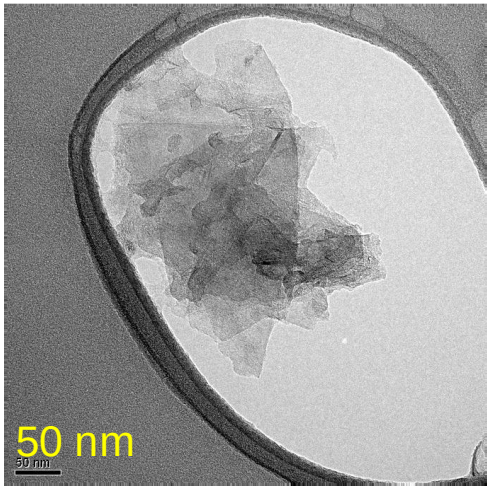
Serinol pyrrole - SP

Functionalization of sp^2 carbon allotropes

sp^2 Carbon allotropes (CA)



The graphitic substrate: nanographite

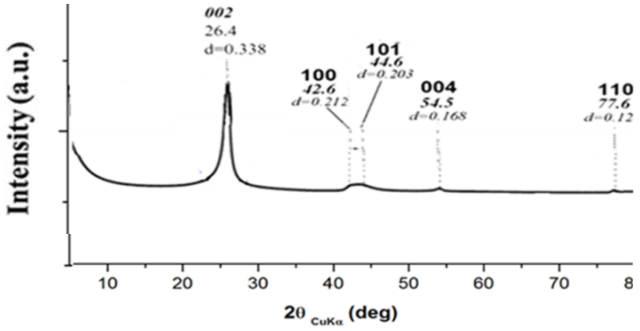


High surface area graphite (HSAG)

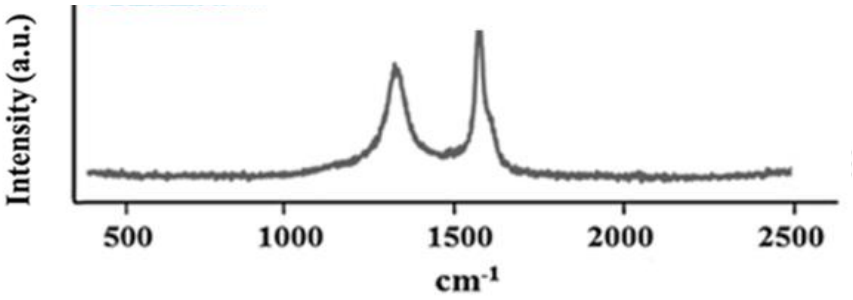
Surface area: 300 m2/g

Number of stacked layers: ca 35

WAXD

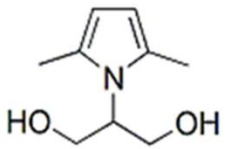


Raman



Mauro M., Cipolletti V., Galimberti M., Longo P., Guerra G., J. Phys. Chem. C, 2012, 116, 24809−24813

CA-SP Adducts - Preparation



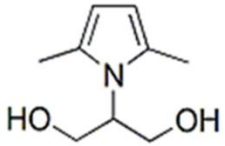
CA + SP

SP = 1 – 20 phc

phc = per hundred carbon

Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G.,Citterio, US 2017 0275169 A1
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

CA-SP Adducts - Preparation



Mechanical treatment

Ball Milling:

300 rpm, 6h

CA/SP-M

CA + SP

SP = 1 – 20 phc

phc = per hundred carbon

Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
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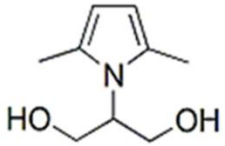
CA-SP Adducts - Preparation



Mechanical treatment

Ball Milling:

300 rpm, 6h

CA/SP-M

CA + SP

SP = 1 – 20 phc

phc = per hundred carbon

80 - 180 C

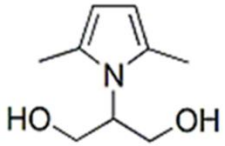
0,5 - 4 h

CA/SP-T

Thermal treatment

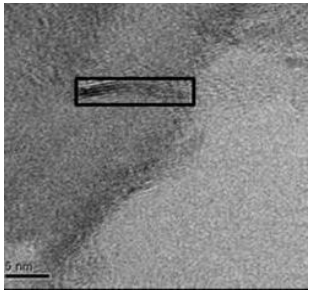
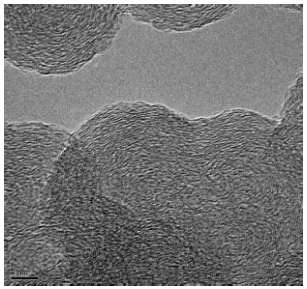
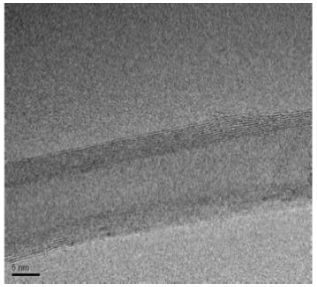
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G.,Citterio, US 2017 0275169 A1
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

CA-SP Adducts - Yield of functionalization*



Thermal treatment

SP = 5 phc; 150°C, 2 h

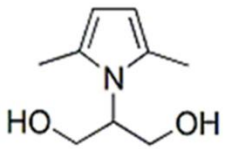
	HSAG	CB	MWCNT
			
BET Surface area: [m^2/g]	300	77	275
Functionalization Yield(%)*:	96	82	92

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

from TGA

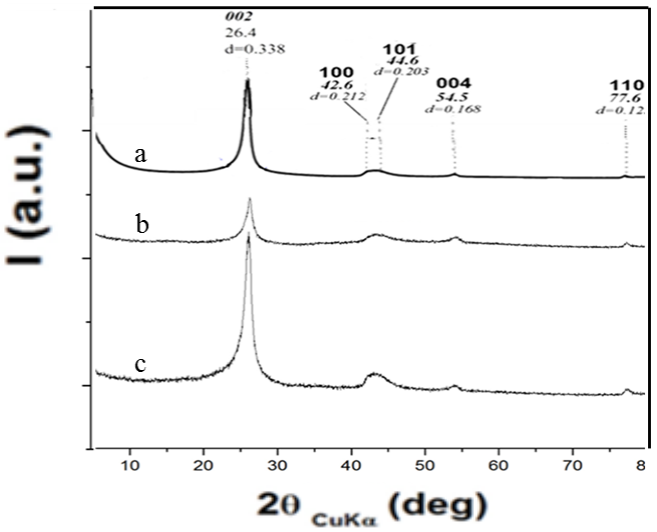
HSAG from Asbury, CB from Cabot, CNT from Nanocyl

Adducts of SP with high surface area graphite (HSAG)



CA/SP → Soxhlet extraction in acetone

WAXD

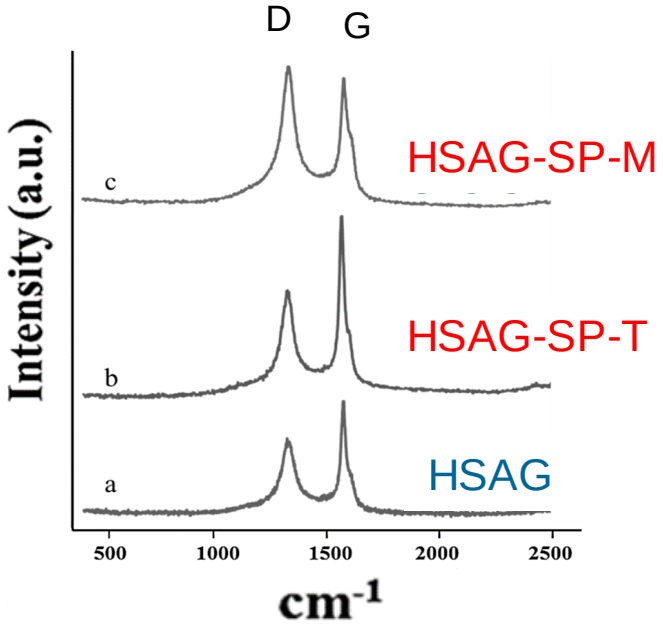


HSAG

HSAG-SP-M

HSAG-SP-T

Raman



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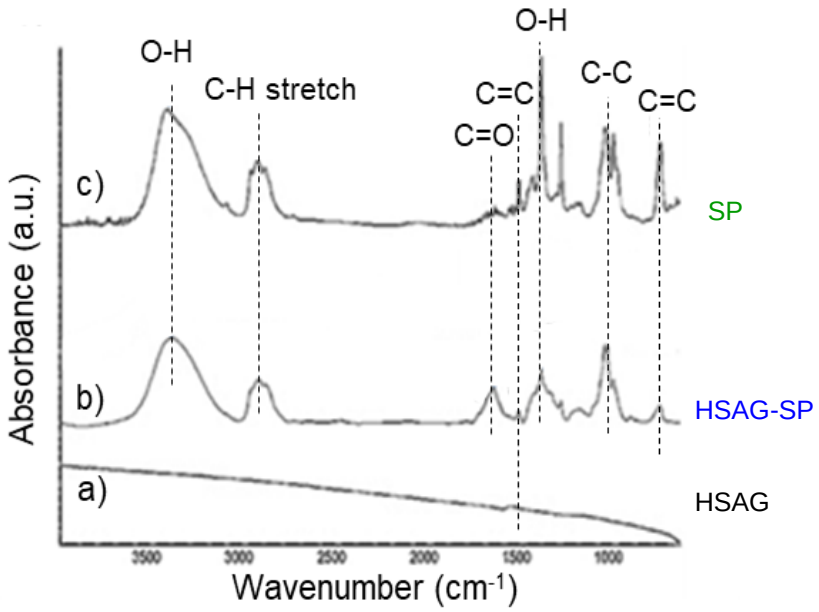
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

Adducts of SP with high surface area graphite (HSAG)

CA/SP-T → Soxhlet extraction in acetone

FT-IR



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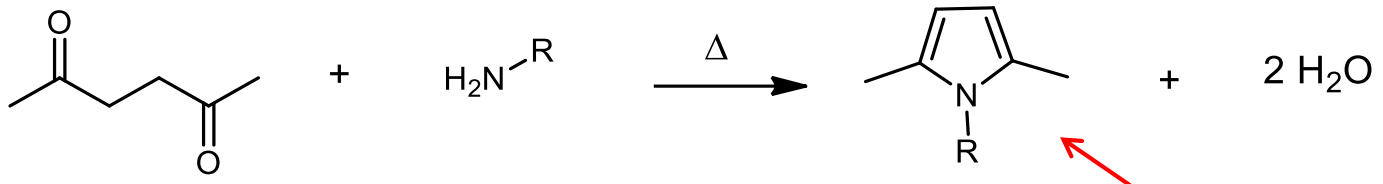
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

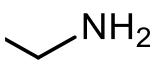
Pyrrole compounds (PyC) from neat Paal Knorr reaction



Same reaction conditions used for SP

PyC

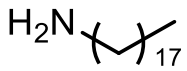
Yield %



80

75

62



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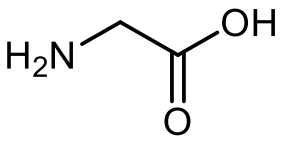

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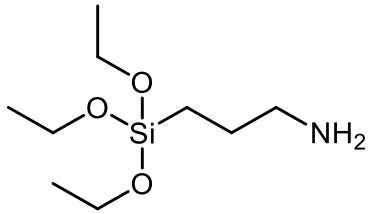

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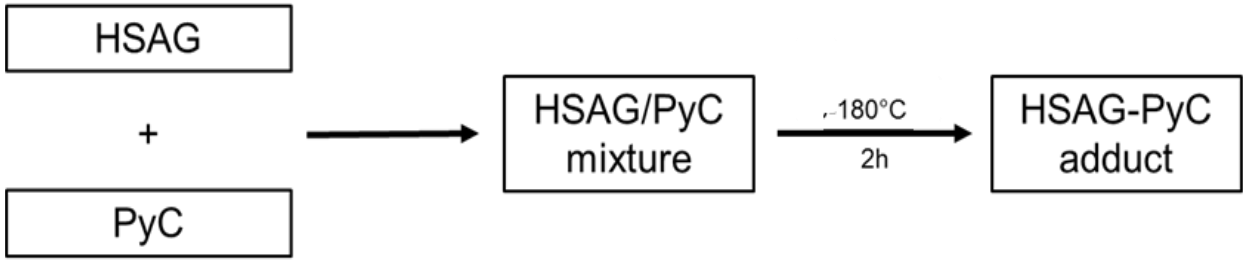
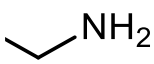
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

HSAG / PyC adducts



Functionalization Yield %



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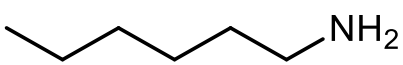

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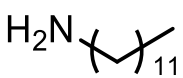

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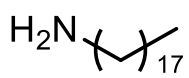

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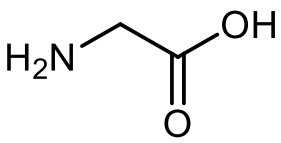

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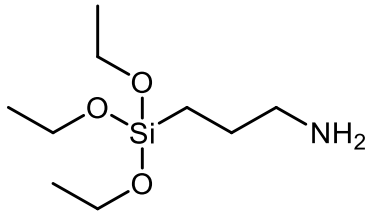
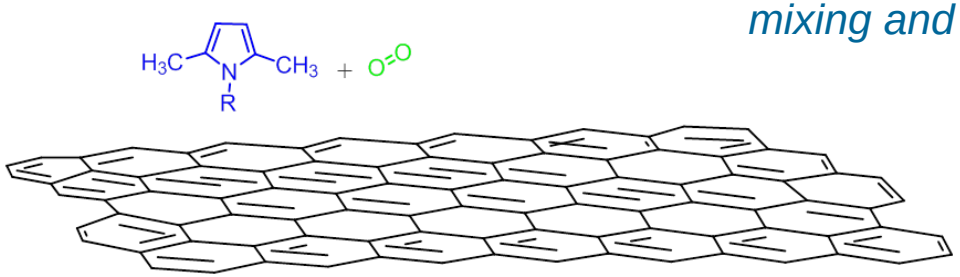


70

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

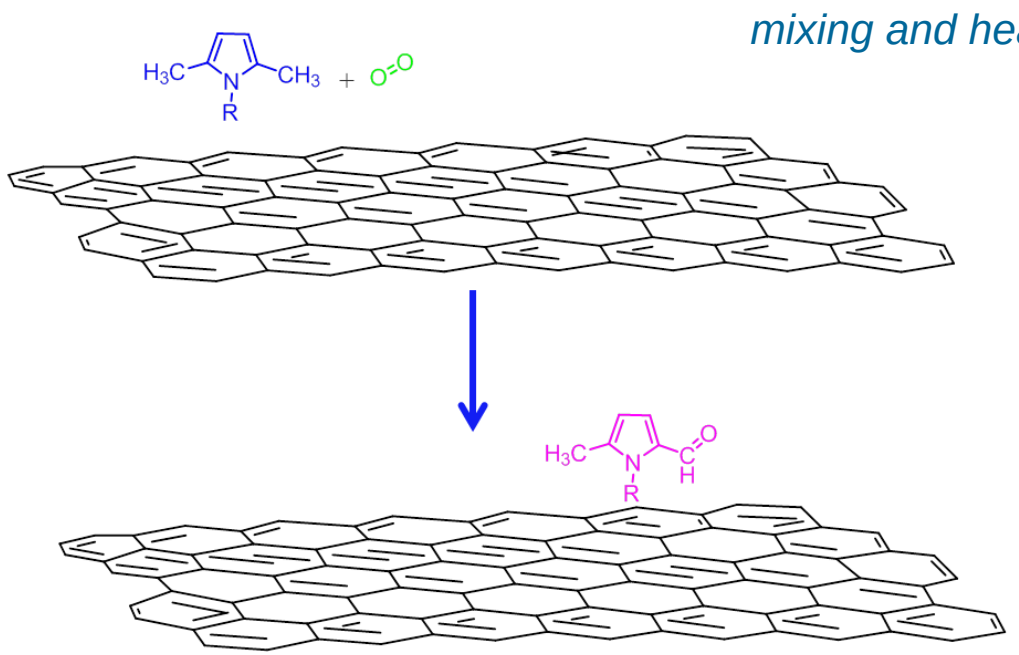
Mechanism for the formation of CA/PyC adducts

mixing and heating



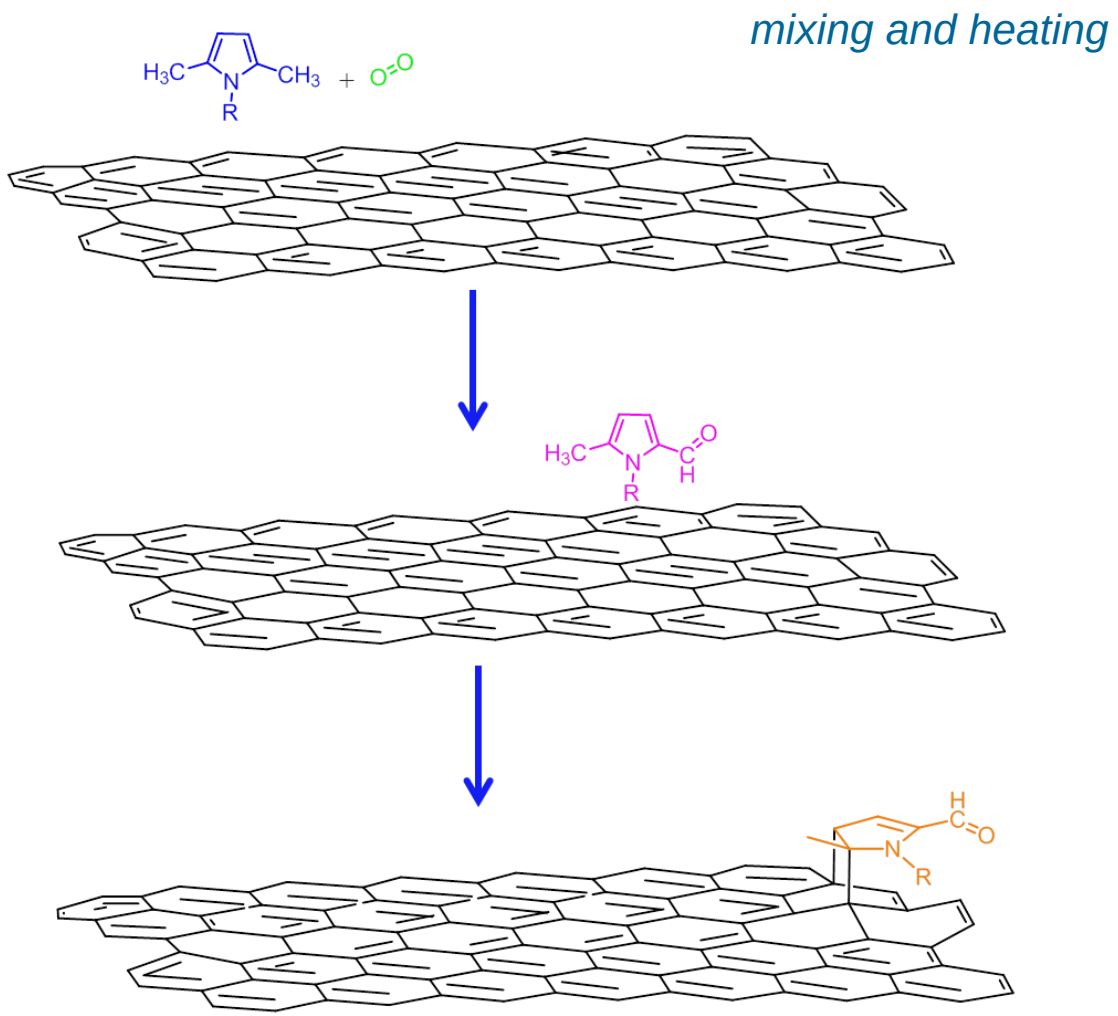
V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

Mechanism for the formation of CA/PyC adducts



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

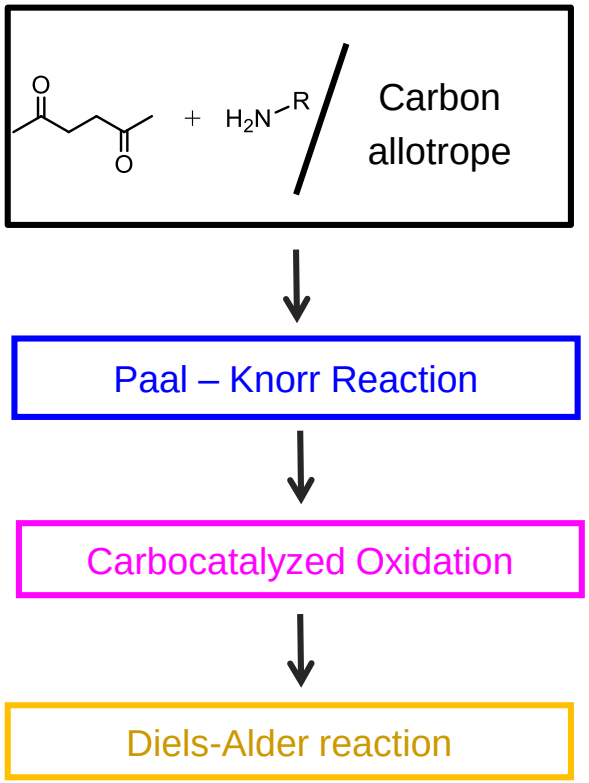
Mechanism for the formation of CA/PyC adducts

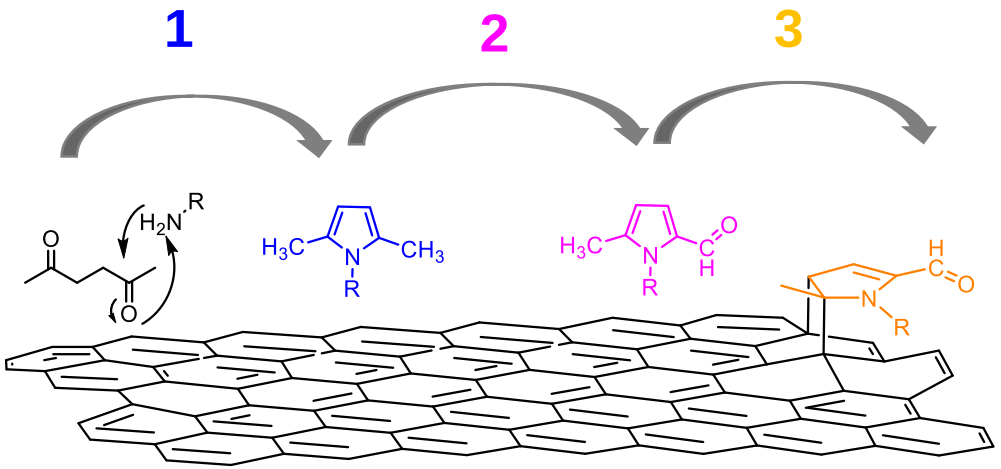


V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

Mechanism for the formation of CA/PyC adducts

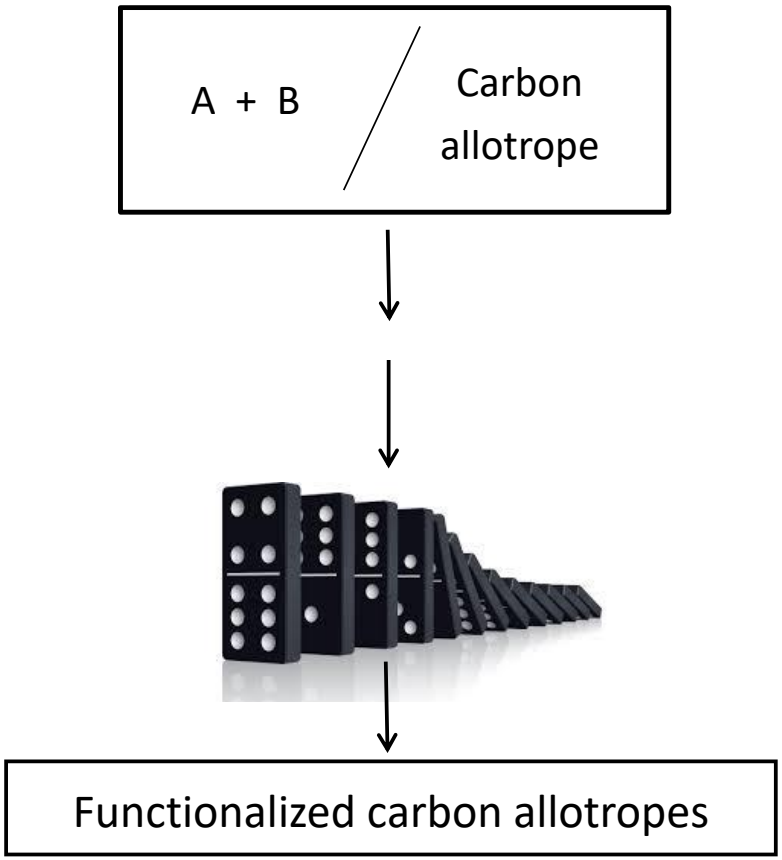
Domino reaction





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

The CA/PyC adducts



- Functional group:
  from few % to 20%
- Functionalization yield:
  from 85% to quantitative
- Covalent bond
  between functional group and carbon allotrope
- Bulk structure of graphitic materials:
  substantially unaltered

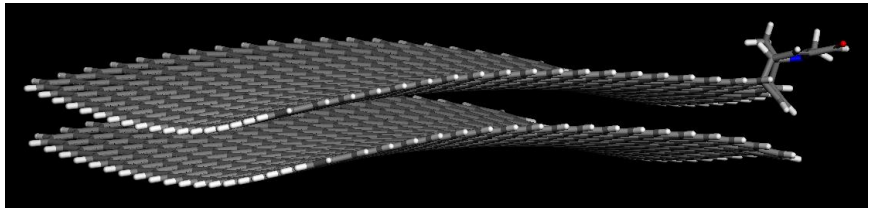
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. *US10329253B2*
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. *US10160652B2*
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. *EP3180379B1*
M. Galimberti, V. Barbera, *EP3538511A1*
M. Galimberti, V. Barbera, *EP3538481A1*

The covalent and supramolecular interaction of PyC with graphene layers

Theoretical study based on Molecular Mechanics
and Molecular Dynamics simulations of:

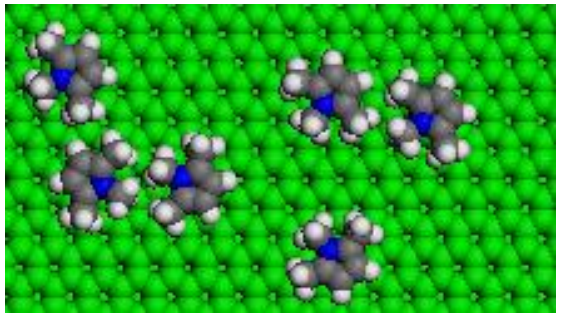
- Few layers of *nano*graphene

☞ importance of covalent functionalization



- Adsorption of pyrrole compound

☞ role of π-π interactions

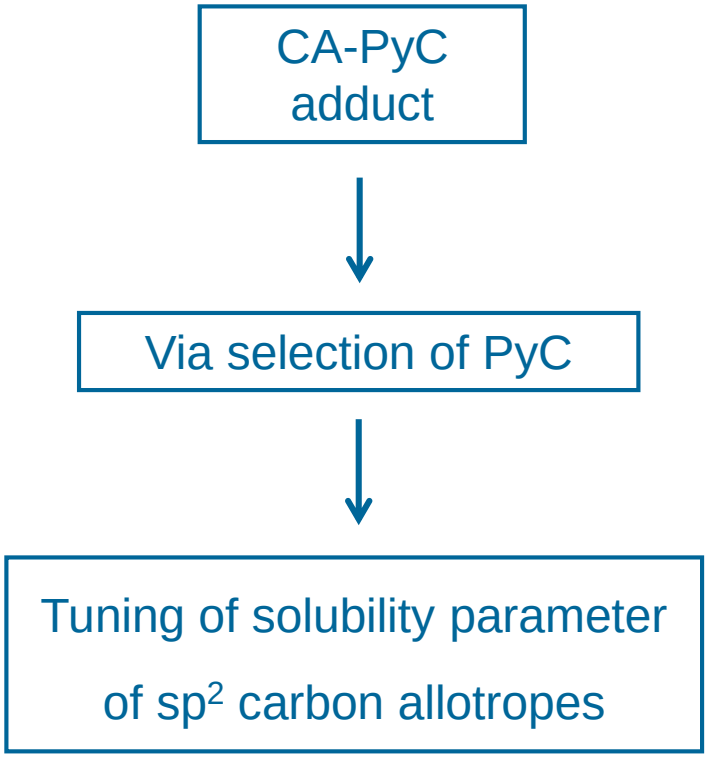


Work in progress…

Raffaini, G.; Ganazzoli, F. ***Macromol. Biosci.*** **2007, *7*, 552.**
Understanding the performance of biomaterials through molecular modeling: Crossing the bridge between their intrinsic properties and the surface adsorption of proteins

Tuning of solubility parameter of sp^2 carbon allotropes

Tuning of solubility parameter of sp^2 carbon allotropes



CA / PyC adducts - Tuning of solubility parameters

Experimental determination

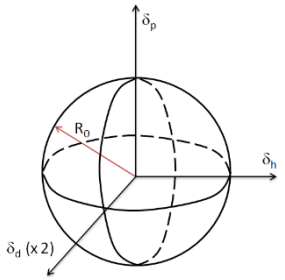
↓

Stable suspensions
in solvents
with different δ

Theoretical predictions

↓

Computational model:
Hansen solubility parameters



Evaluation of solubility parameters of HSAG-PyC - Experiments

Adduct	solvents				
HSAG-	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**

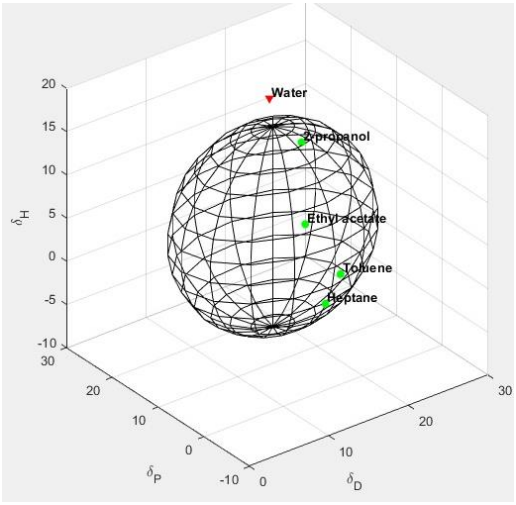
Unstable suspension: **bad**

Stable suspension: **good**

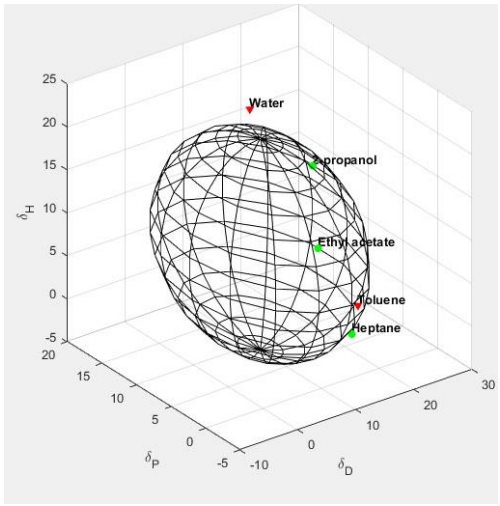
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

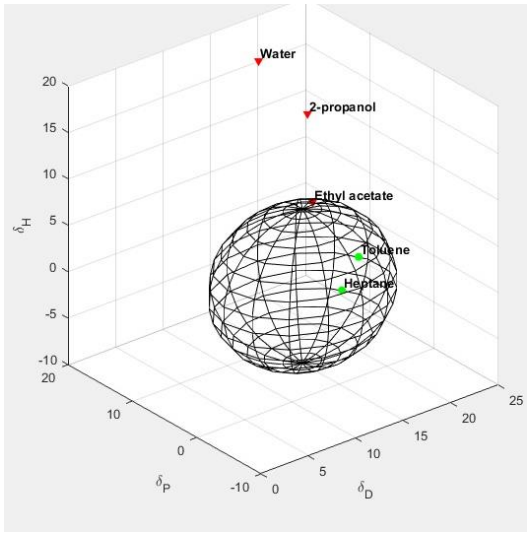
HSAG-TMP



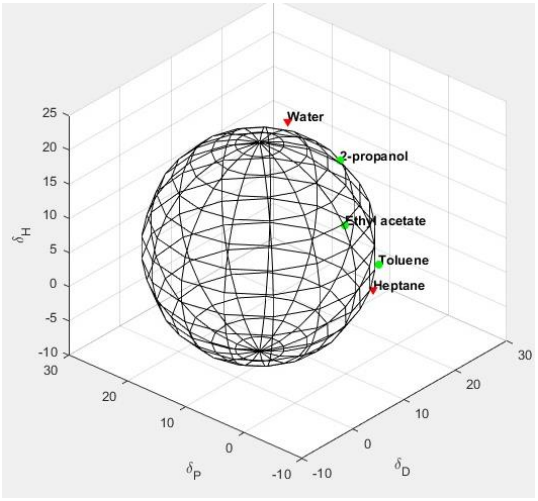
HSAG-DDcP



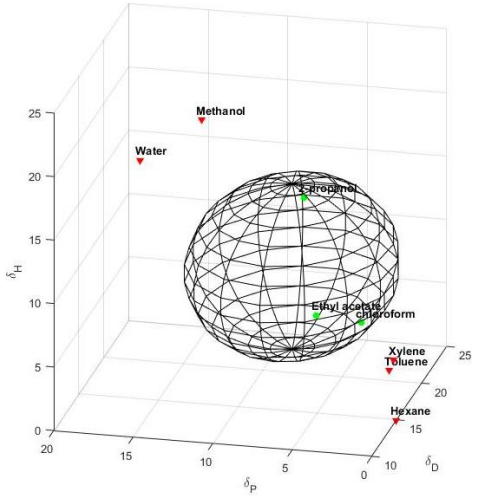
HSAG-APTESP

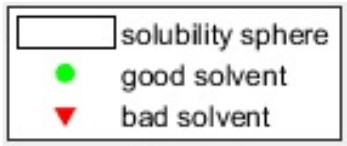


HSAG-GlyP



HSAG-SP



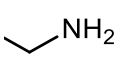


V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

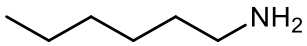
Evaluation of solubility parameters of HSAG-PyC - δ values

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

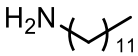
Amount of PyC on HSAG: about 5% mol



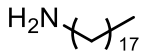
TMP



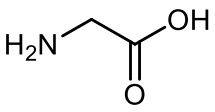
EP



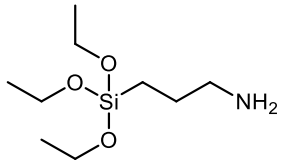
DDcP



ODcP



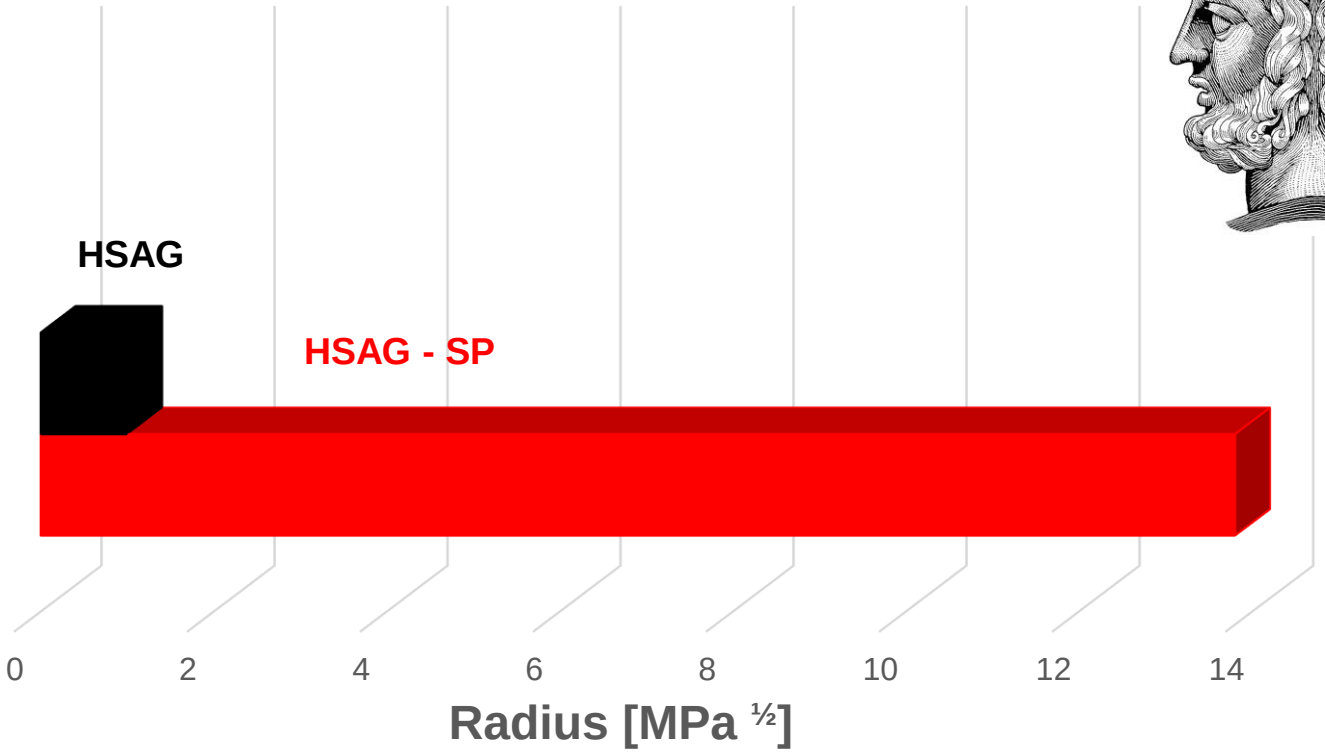
GlyP



APTESP

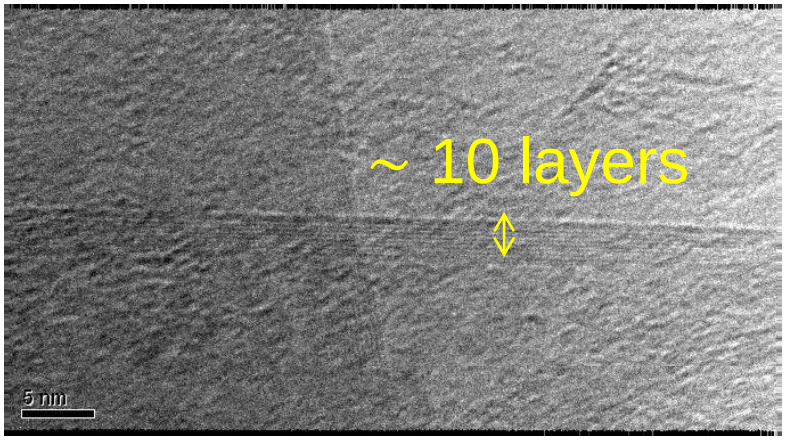
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

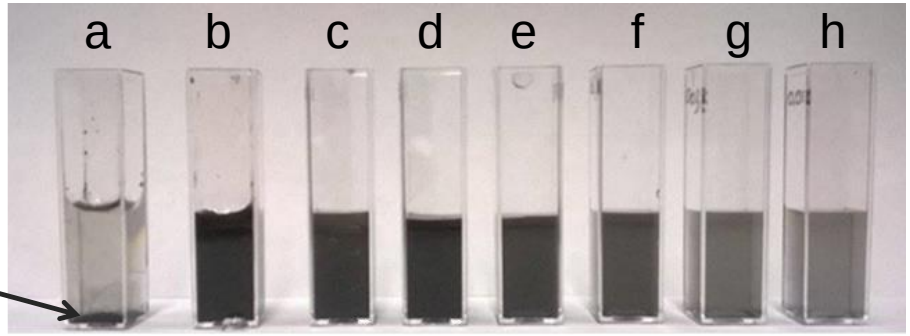
HSAG and HSAG/SP - Hansen sphere radius comparison



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

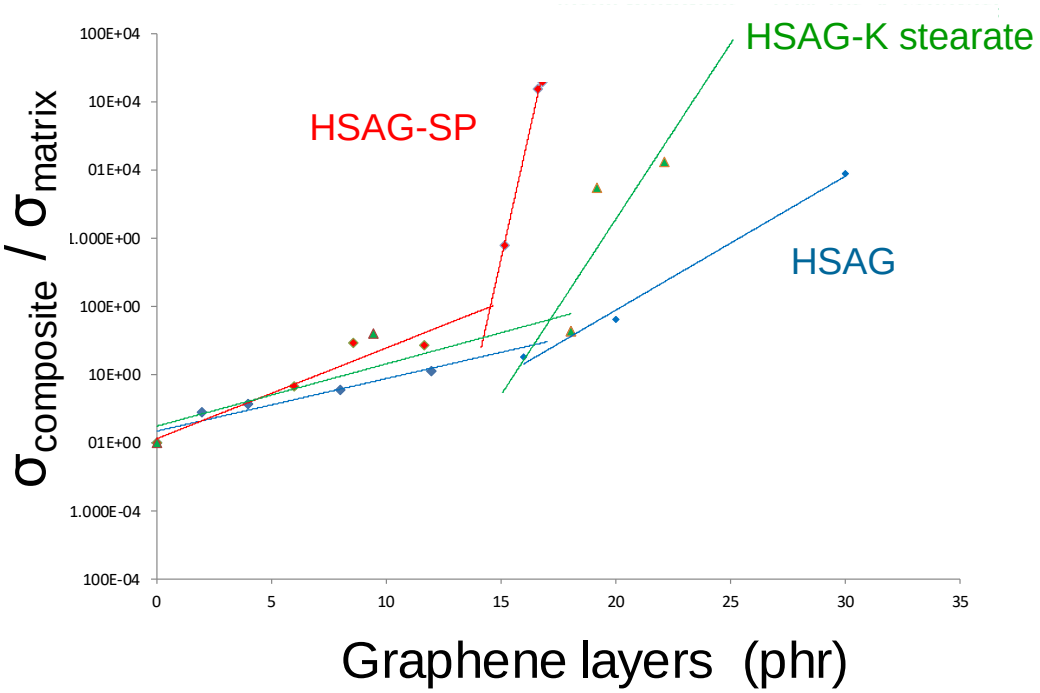
Production of few layers graphene





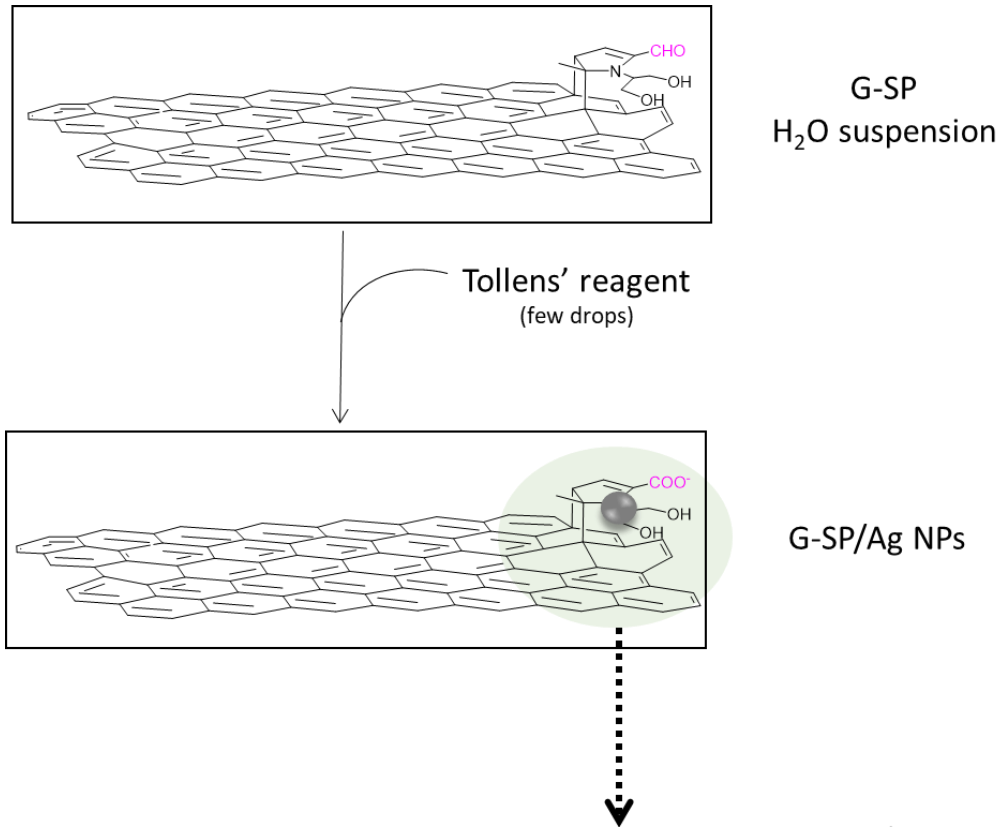
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini *RSC Adv., 2015, 5, 81142-81152*

Electrically conductive coating layers



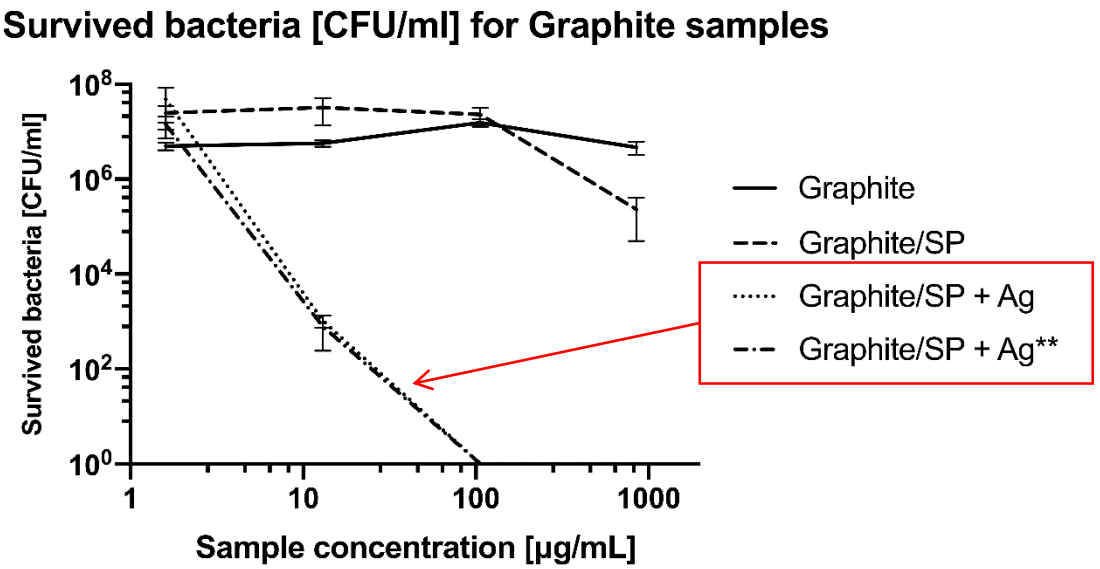
S. Guerra, V. Barbera, M. Galimberti, U. Giese, *KGK 2020, 04, 17-25*

Antibacterial additives



Antibacterial additive

Antibacterial activity



**The sample has been functionalized with an almost double quantity of Tollens' reagent.

Test: ASTM Standard Guide E2315 – 16

Bacteria: E. coli JM109 – DSM3423

Material state: Dispersions of powders

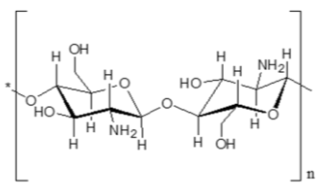
Inoculum concentration: ~10^6 CFU/mL

Culture medium: LB / PBS 1:100 (v/v)

Culture conditions: 24h, 37°C, 5% CO_2, 90% R.H. Dynamic conditions

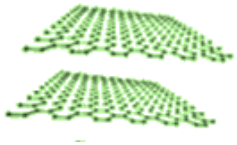
V. Barbera, M. Galimberti, G. Candiani, *Italian Patent Application n. 102020000020113*

Bionanocomposites



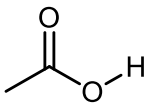
Poly(D-glucosamine)
Chitosan (CS)

+

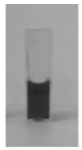


HSAG-SP adduct

+



Acetic acid



HSAG-SP/CS Water solution

by casting
the water solution

freeze-dry method

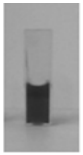
Carbon papers

Aerogels

V. Barbera, S. Guerra, L. Brambilla, M. Maggio, A. Serafini, L. Conzatti, A. Vitale, M. Galimberti, *Biomacromolecules, 2017, 18 (12), 3978–399*

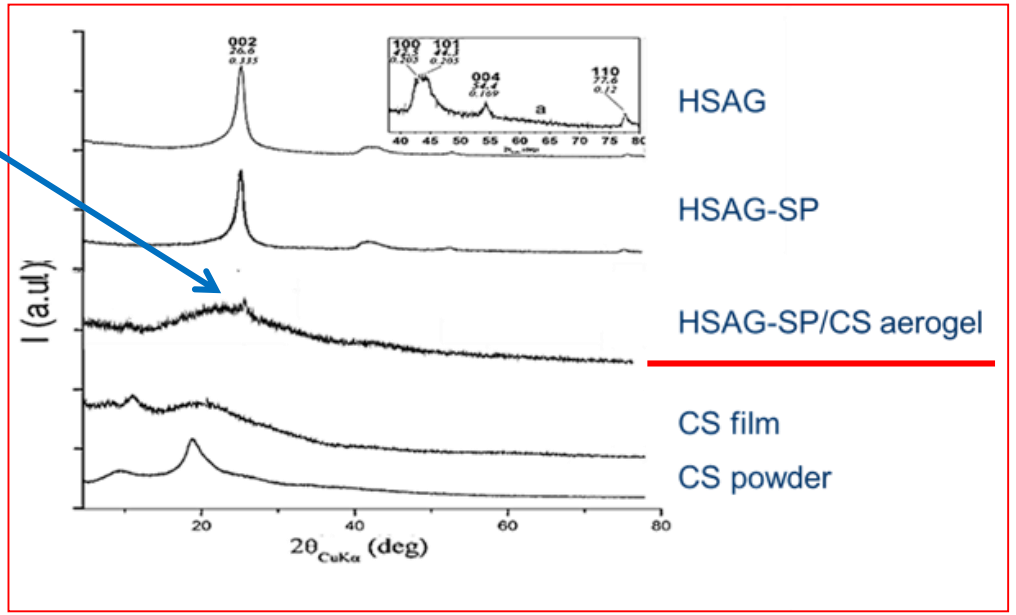
S. Guerra, V. Barbera, A. Vitale, R. Bongiovanni, A. Serafini L. Conzatti, L. Brambilla, M. Galimberti, *Materials 2020, 13, 39*

Bionanocomposites



freeze-dry method

Monolithic aerogel



V. Barbera, S. Guerra, L. Brambilla, M. Maggio, A. Serafini, L. Conzatti, A. Vitale, M. Galimberti, *Biomacromolecules, 2017, 18 (12), 3978–399*

S. Guerra, V. Barbera, A. Vitale, R. Bongiovanni, A. Serafini L. Conzatti, L. Brambilla, M. Galimberti, *Materials 2020, 13, 39*

C6 building blocks

Sugars from hydrolyzed biomass

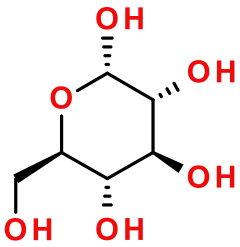
Biomass
for energy uses

Bio-ethanol

Biomass
for materials

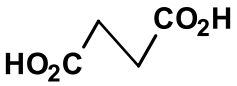
Polysaccharides

Chemicals from sugar

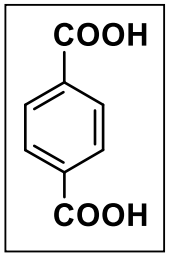


D-glucose

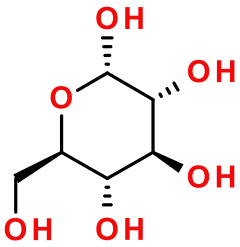
Chemicals from sugar - Target molecules



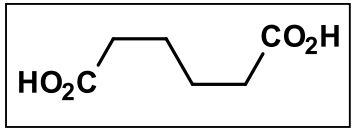
succinic acid



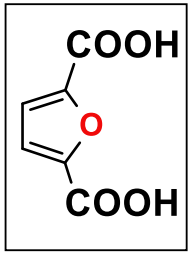
terephthalic acid



D-glucose

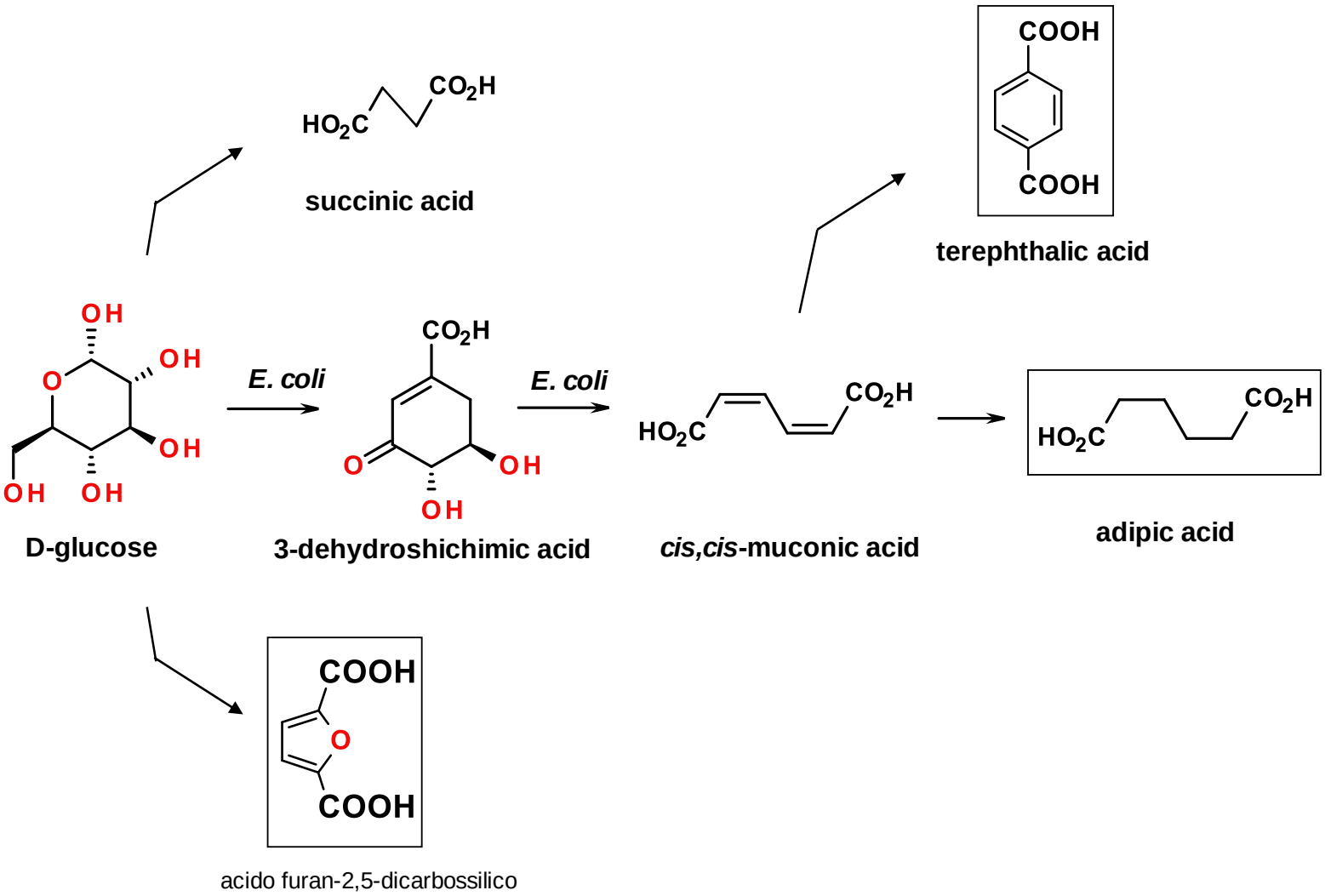


adipic acid

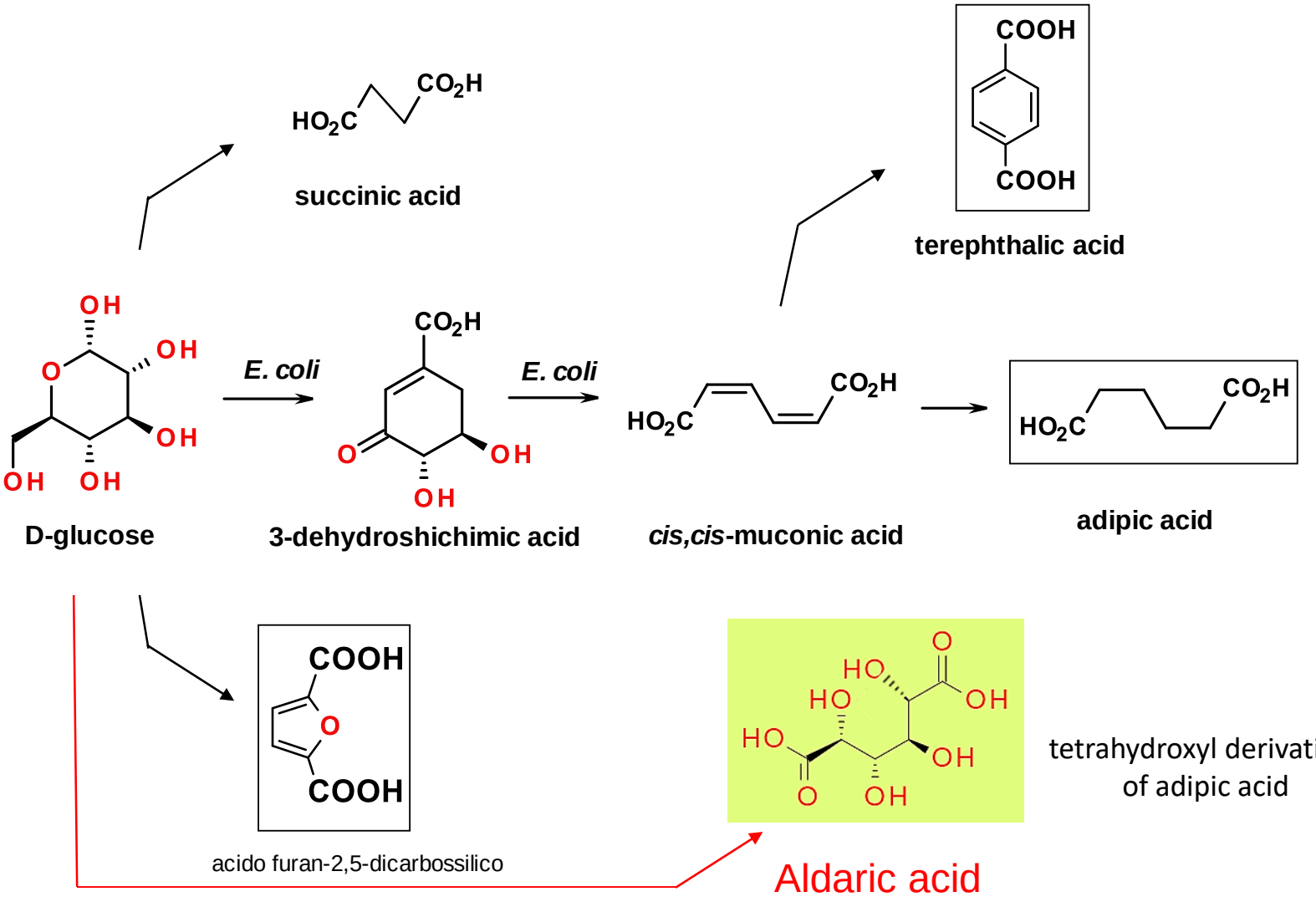


acido furan-2,5-dicarbossilico

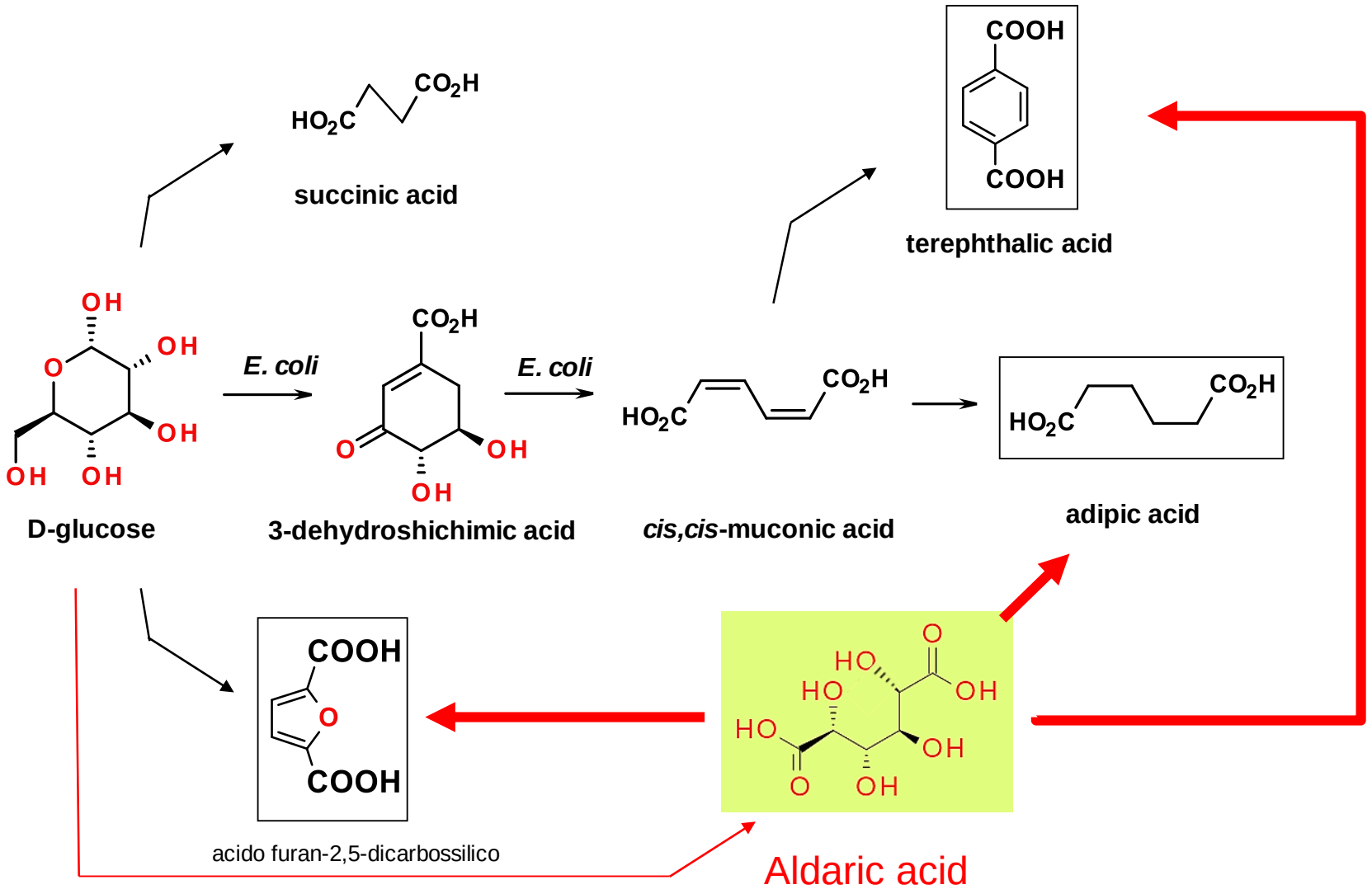
Chemicals from sugar - Target molecules



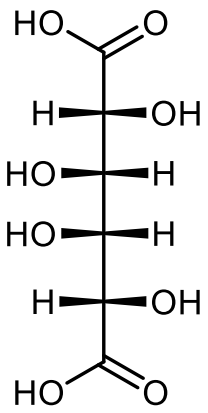
Dicarboxylic Acids from Hydrolyzed Biomasses



Dicarboxylic Acids from Hydrolyzed Biomasses

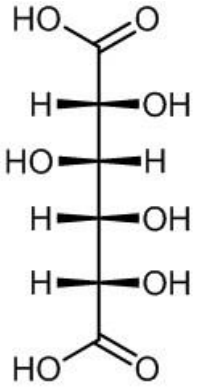


Aldaric acids as platform chemicals



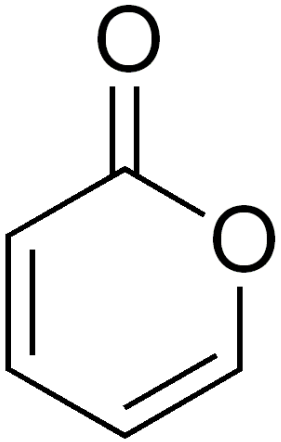
Mucic
(galactaric)

$C_6H_{10}O_8$



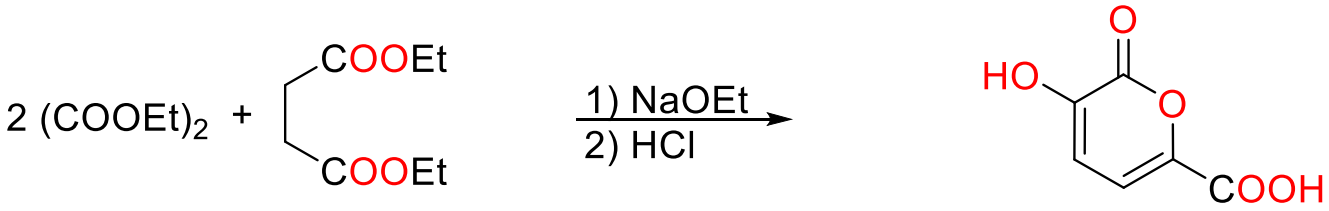
D-Glucaric

From aldaric acids to pyrones

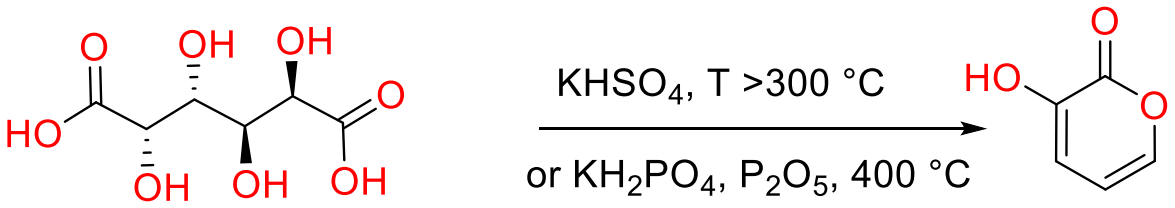


From aldaric acids to pyrones - Prior art

Yield

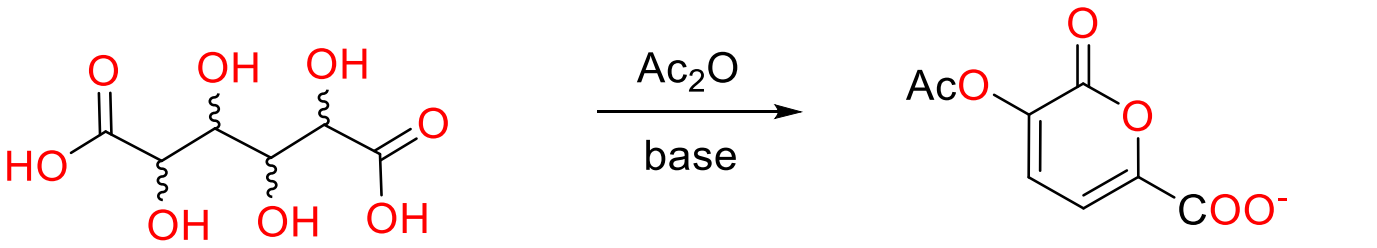


up to10%



11 - 40%

Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP

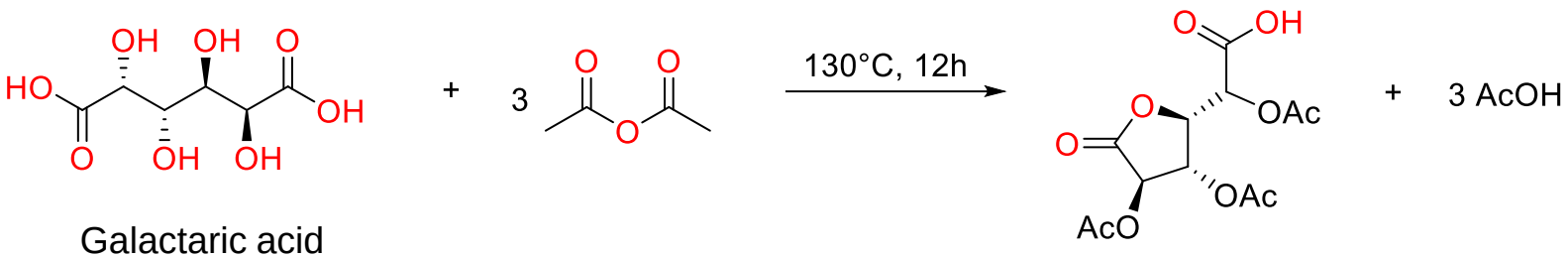


3-Acetoxy-2-oxo-2*H*-pyran-6-carboxylic salt (GAB-OAc)

- Easy procedure
- No solvent
- No catalyst
- High Conversion
- High Atom efficiency

Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP

First step

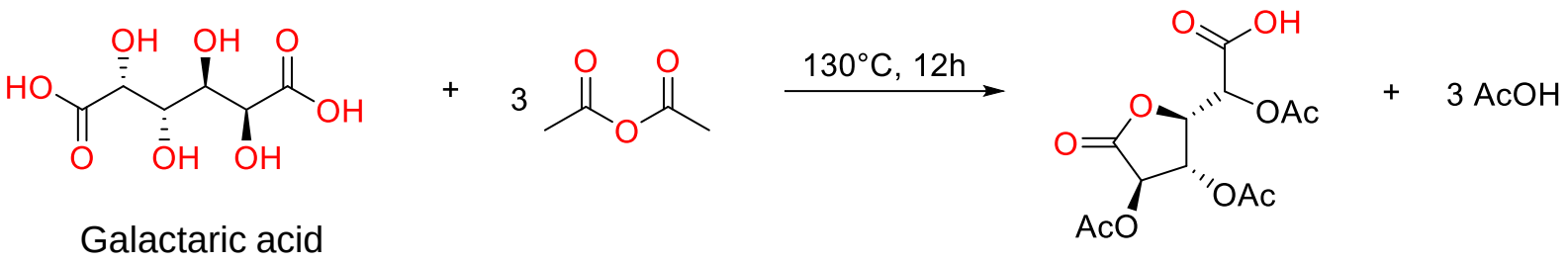


Galactaric acid

Yield = 99%; A.E. = 77%

Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP

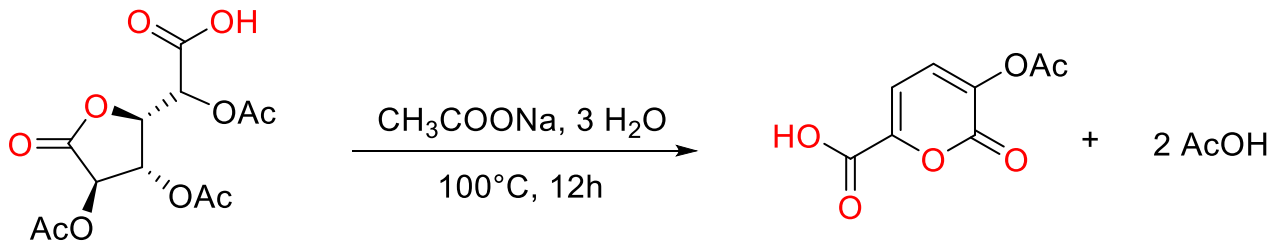
First step



Galactaric acid

Yield = 99%; A.E. = 77%

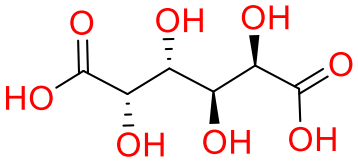
Second step



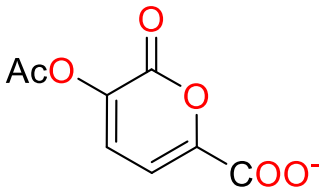
Yield = 65%; A.E. = 62%

Leonardi G., Li, J., Righetti, G. I. C., Truscello, A. M., Gambarotti, C., Terraneo, G., Citterio, A., Sebastiano, R., *Eur. J. Org. Chem.* **2020**, 241–251

Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP

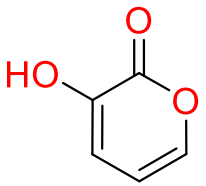


Galactaric acid



GAB-OAc

Yield
up to 73%

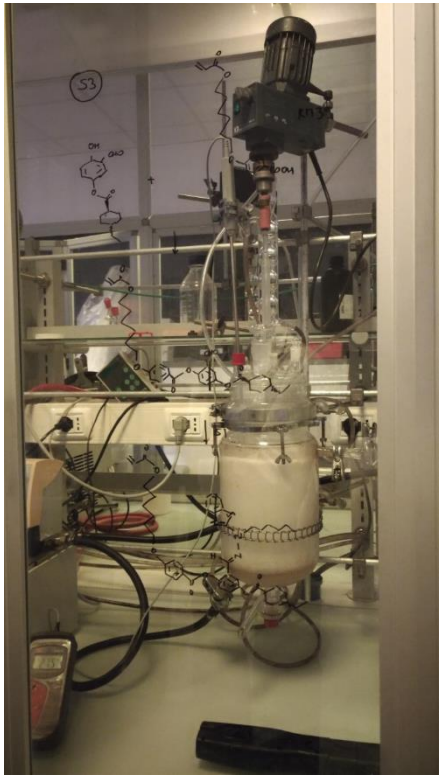


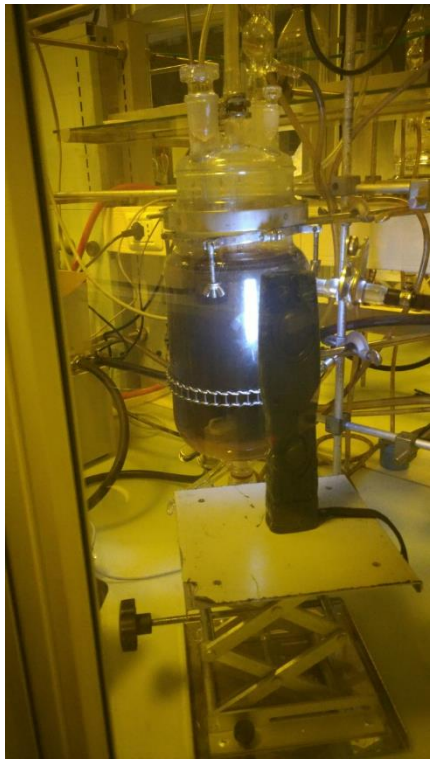
DEC

Yield
up to 90%

Leonardi et al. *Eur. J. Org. Chem.* **2020**, 241–251

Synthesis of Pyrone - Scale up





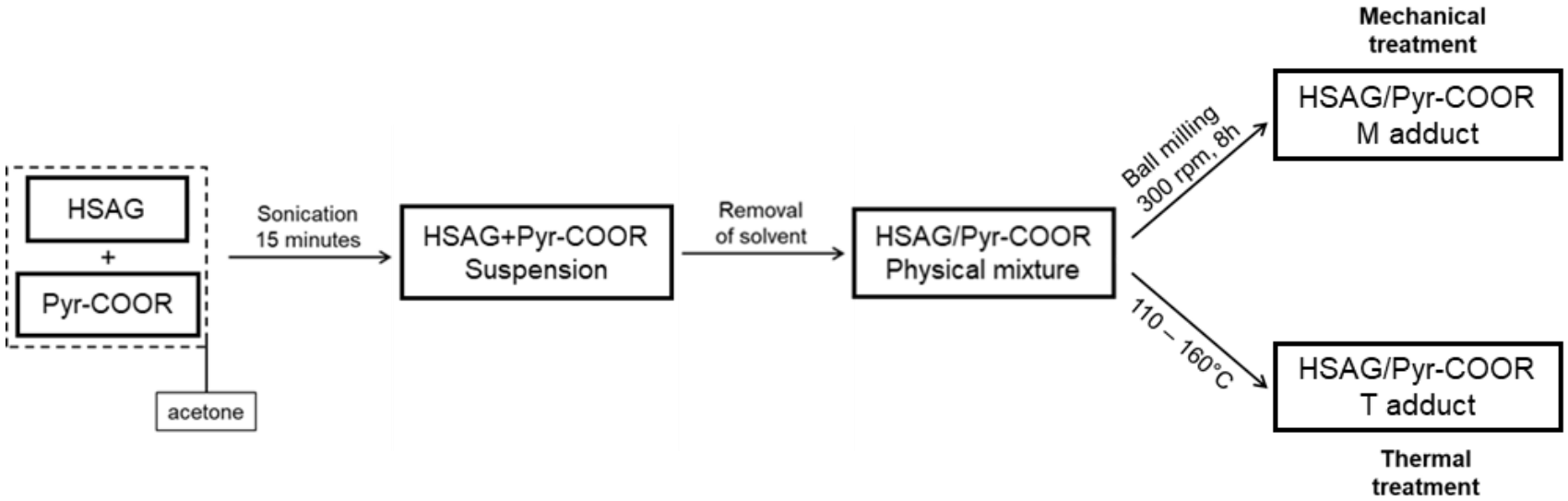
One Pot

2 hours

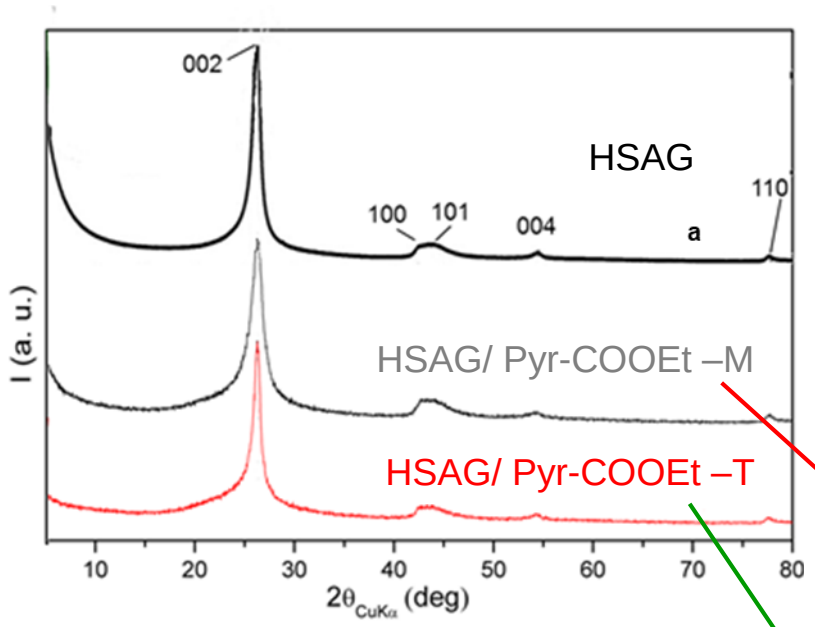
Yield = 75%

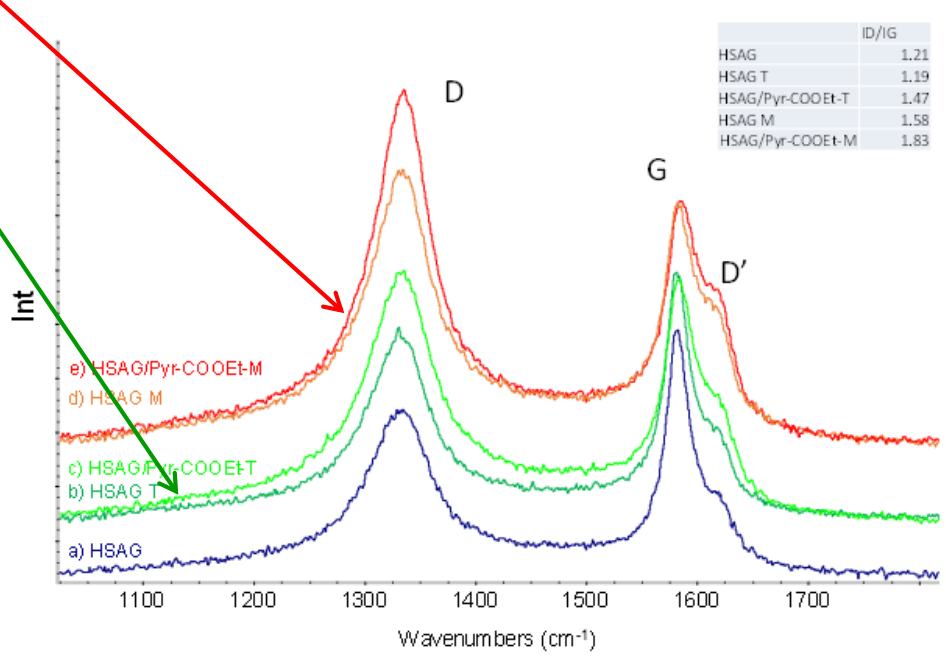
Functionalization of sp^2 carbon allotropes

Functionalization of HSAG with a Pyrone derivative

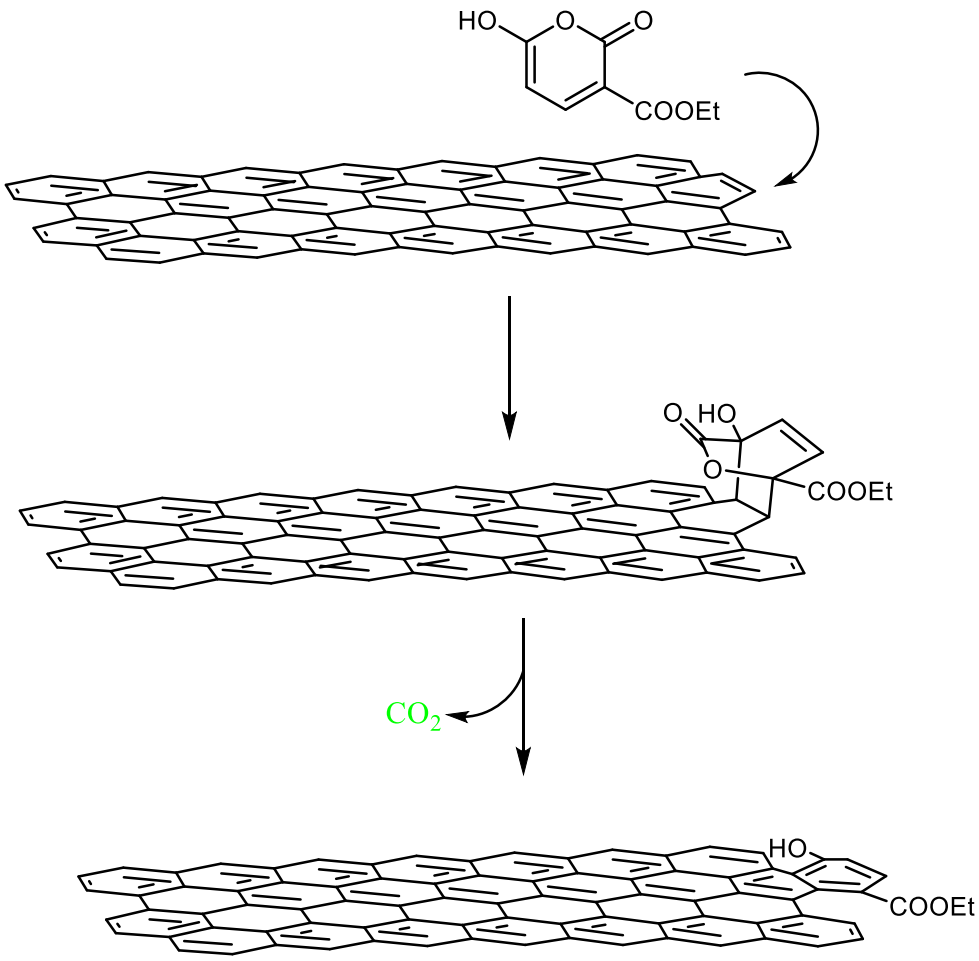


Adduct of HSAG with Pyr-COOEt





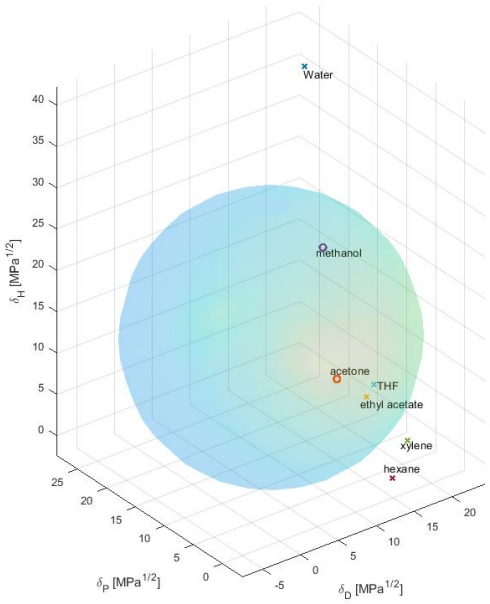
EDGE-GO - Functionalization of HSAG with a Pyrone derivative



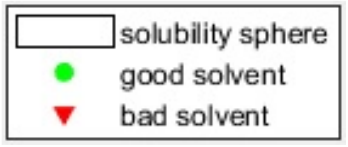
Evaluation of solubility parameters of HSAG-Pyr-COOEt

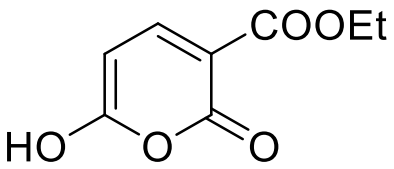
Amount of Pyr-COOEt on HSAG: about 5% mol

solvents						
water	acetone	methanol	isopropanol	ethyl acetate	toluene	heptane
good	good	good	bad (↓)	bad (↓)	bad (↓)	bad (↓)

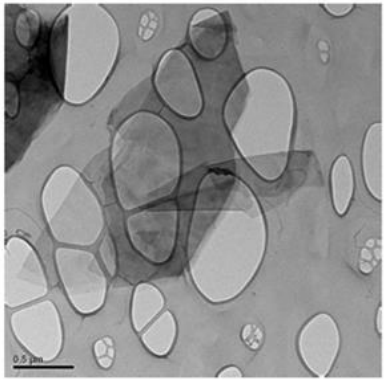


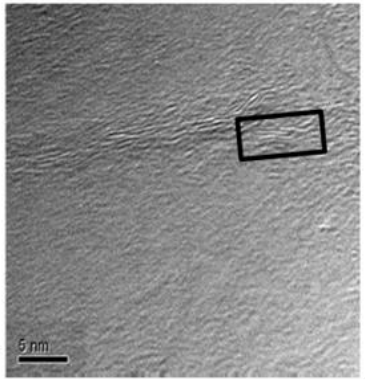
Sample	δ_D	δ_P	δ_H	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-Pyr-COOEt	8.36	12.46	13.59	16.05





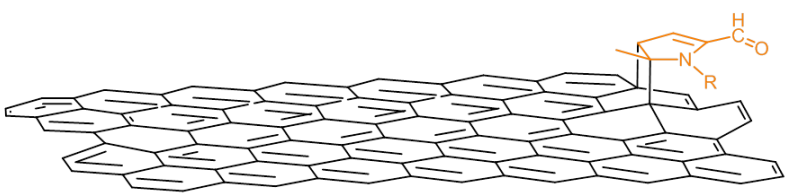
Preparation of few layers graphene

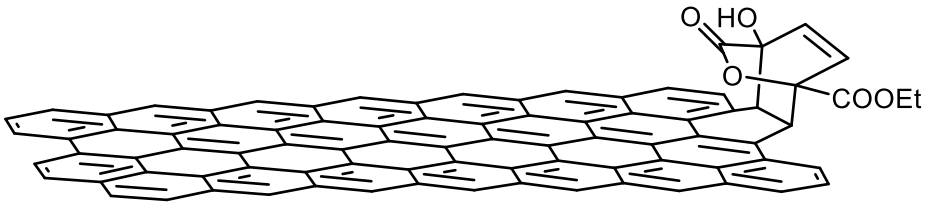


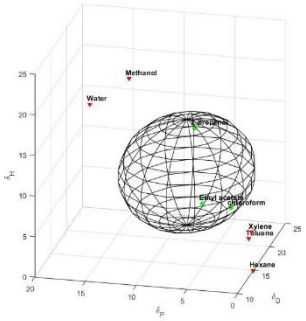


Conclusions

Edge functionalization of graphene layers with biobased molecules







Thanks

for your attention!

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