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A green approach to the edge functionalization of graphene layers with a bio-based 2-pyrone

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IX Workshop AICIng
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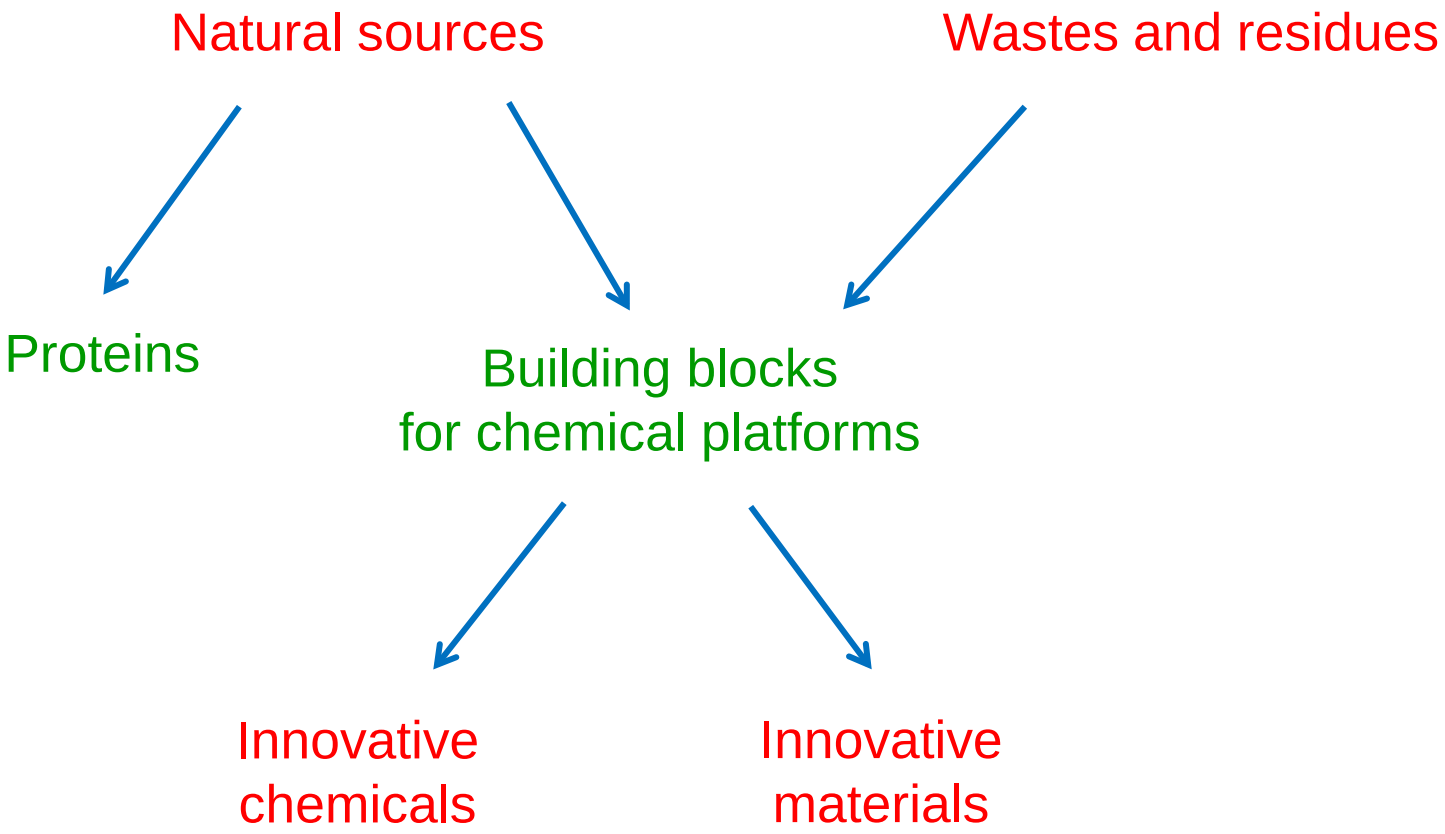
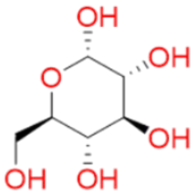


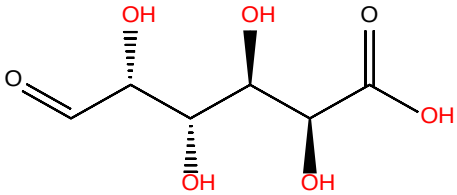
☞ Chemicals, Additives, Modifiers, Polymers

C6 building block: Sugars from hydrolyzed biomass

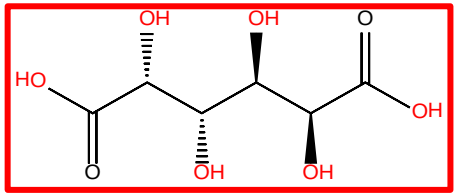
Arundo Donax



D-Glucose

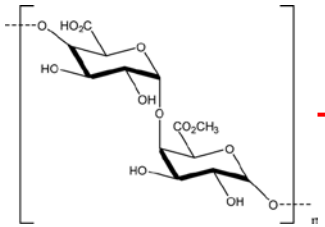


D-Glucuronic Acid



Mucic Acid Or Galactaric Acid

Orange Peels

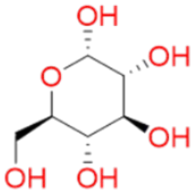


Pectin

- ☞ Symmetrical structure: achiral
- ☞ Platform molecule
- ☞ Not toxic, Biocompatible

C6 building block: from polysaccharides to pyrone compounds

Arundo Donax



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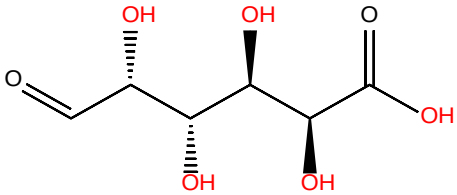
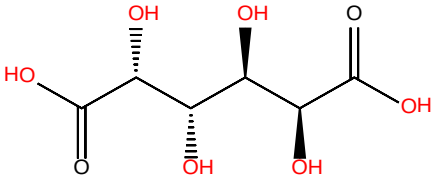
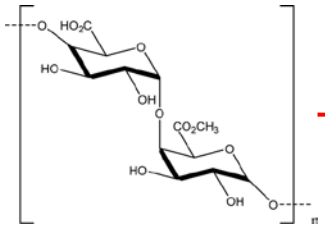


D-Glucuronic Acid

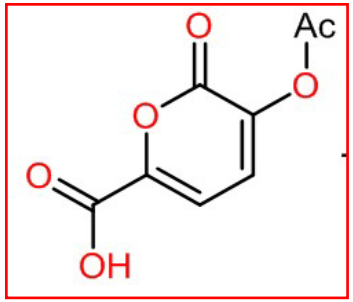


Mucic Acid

Orange Peels



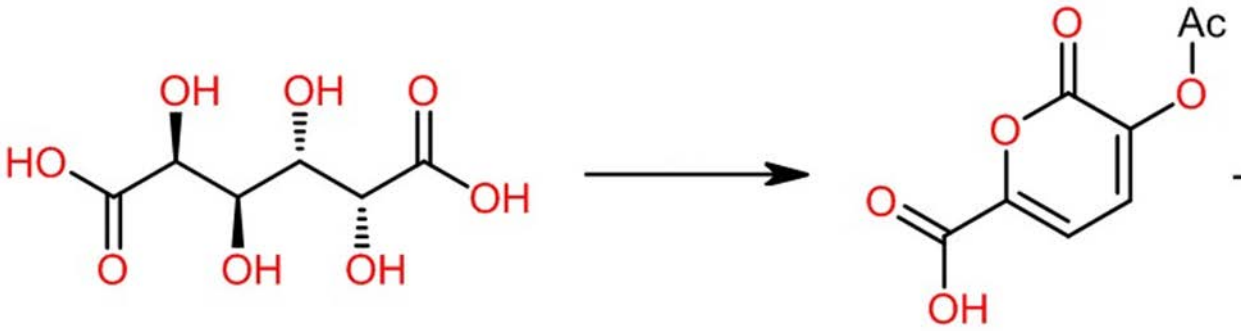
Pectin



2-pyrones

Synthesis of Pyrone Derivatives from Galactaric Acid

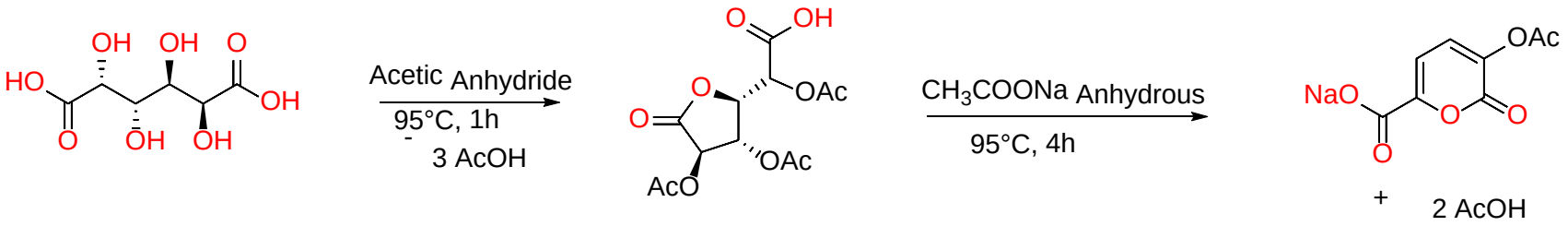
The strategy



- Easy procedure
- No solvent
- High Conversion

Synthesis of Pyrone Derivatives from Galactaric Acid

Reaction scheme for the synthesis of sodium 3-acetoxy-2-oxo-2*H*-pyran-6-carboxylate (Pyr-Na)



Mucic Acid

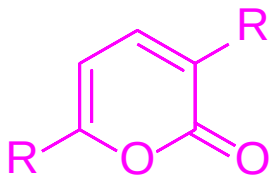
(*S*)-2-acetoxy-2-((2*S*,3*S*,4*R*)-3,4-diacetoxy-5-oxotetrahydrofuran-2-yl) acetic acid

sodium 3-acetoxy-2-oxo-2*H*-pyran-6-carboxylate

Yield

up to 76%

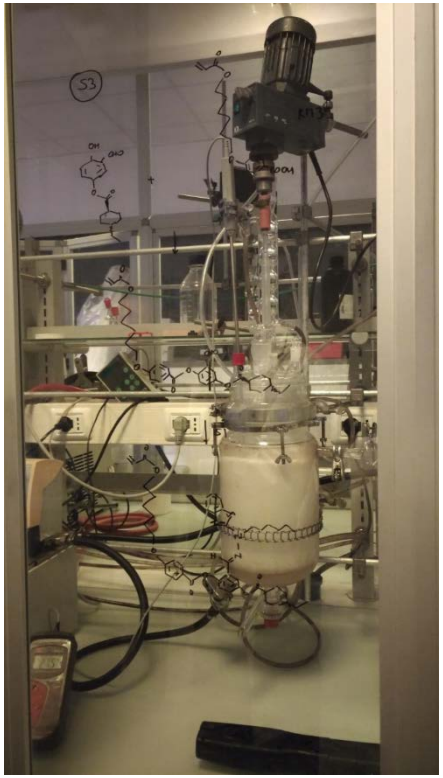
Gabriella Leonardi, Jiemong Li et al - Eur. J. Org. Chem., 2020: 241-251

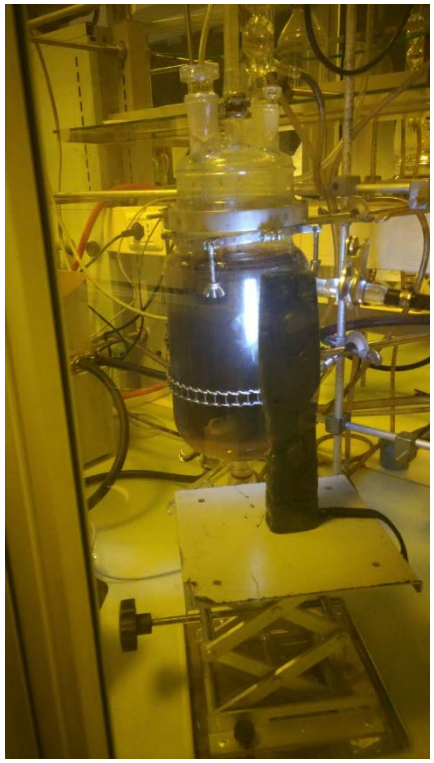


Synthesis of Pyrone:

Scale Up

Synthesis of Pyrone: Scale Up





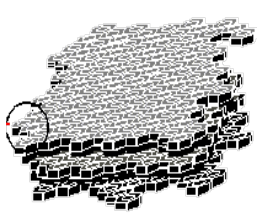
One Pot

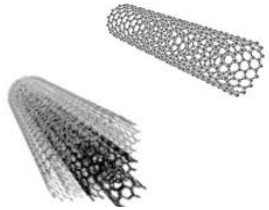
4 hours

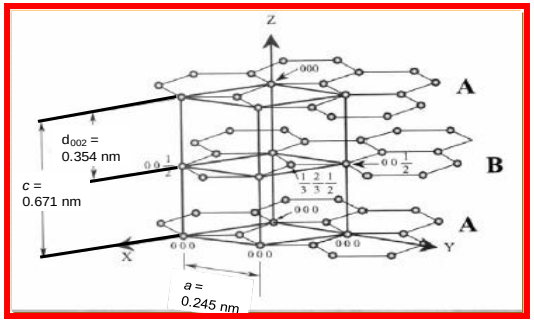
Yield = 75%

300 gr

Functionalization of sp^2 carbon allotropes







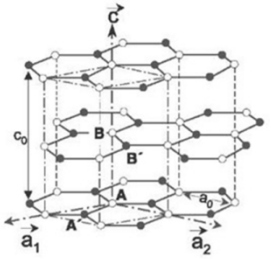
Functionalization of graphene layers

Facile preparation of graphene layers and

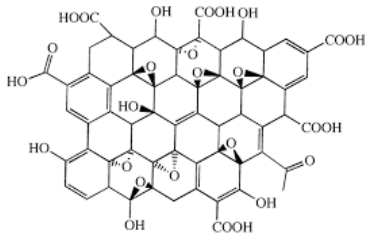
graphene layers with controlled functionalities

is a *Holy Grail* in the field of materials chemistry.

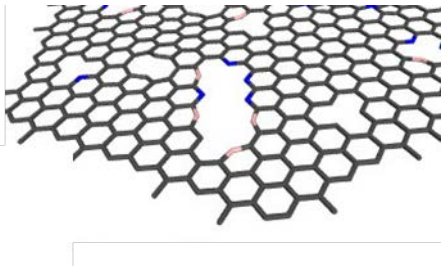
Suitable approach



GO



CRGO

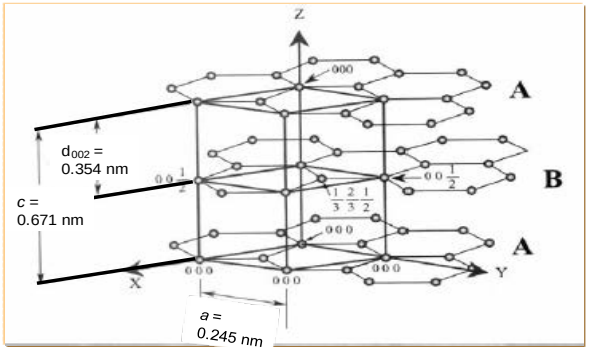


C sp^3 > > sp^2

C sp^2 > > sp^3

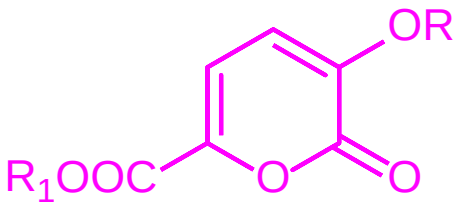
Functionalization of graphene layers

HSAG



+

Pyrones
(Pyr)



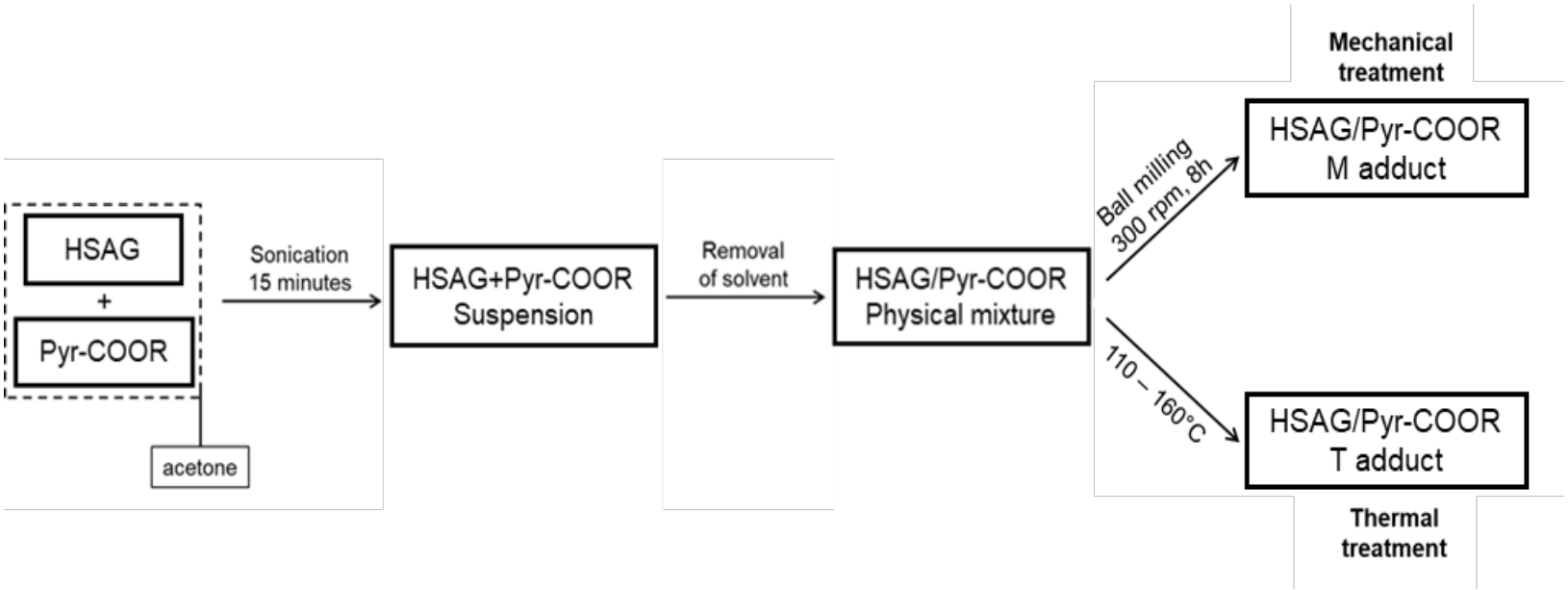
HSAG
=
High Surface Area Graphite
(300 m^2/g)

Main objective

To introduce oxygenated functional groups on HSAG

without altering the bulk crystalline structure of the graphitic substrate

Preparation of adducts of Pyrone with HSAG



Adducts were analyzed through:

1. TGA
2. FT-IR spectroscopy
3. WAXD
4. HRTEM
5. Raman

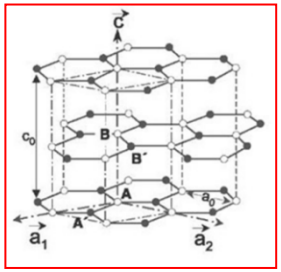
V.Barbera, A. Citterio, M. Galimberti, R. Sebastiano, G. Leonardi, J LI – Italian patent application 2019

F.Margani, M. Magrograssi, M. Piccini, L. Brambilla, V.Barbera, M. Galimberti, – ACS Sustainable Chemistry & Engineering 10, no. 13 (2022): 4082-4093.

Preparation of Adducts of Pyrone with HSAG – Degree of functionalization

Sample	Yield %[a]
HSAG-P/M	85
HSAG-P/T 110°C	81
HSAG-P/T 130°C	83
HSAG-P/T 150°C	82
HSAG-P/T 160°C	91

(a) Determined via TGA

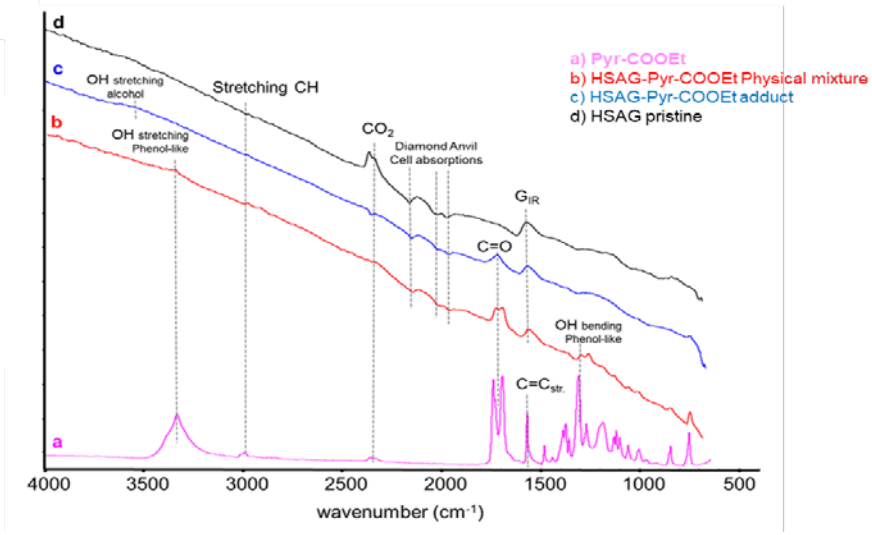


Increasing temperature

- Thermogravimetric Analysis (TGA) reveal a high degree of functionalization

$$Yield = \frac{mass\ of\ the\ adduct\ after\ filtration}{mass\ of\ the\ mixture} * 100\%$$

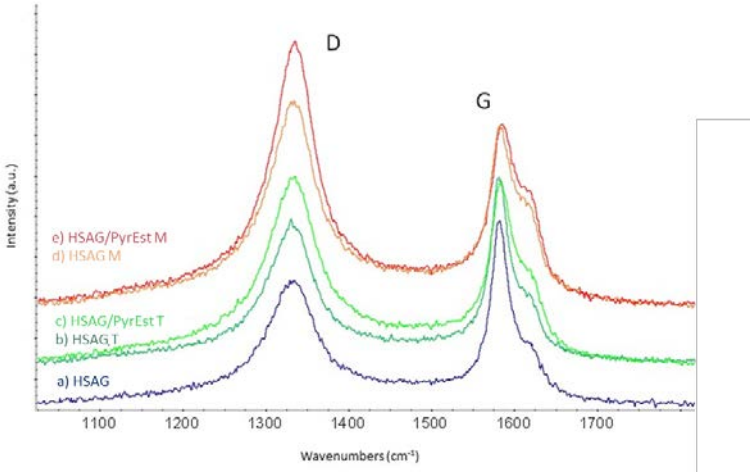
Characterization of Adducts – FT-IR and Raman



In the spectra
of HSAG/ Pyr-COOEt adducts
a new signal at 1729 cm^{-1} appears.

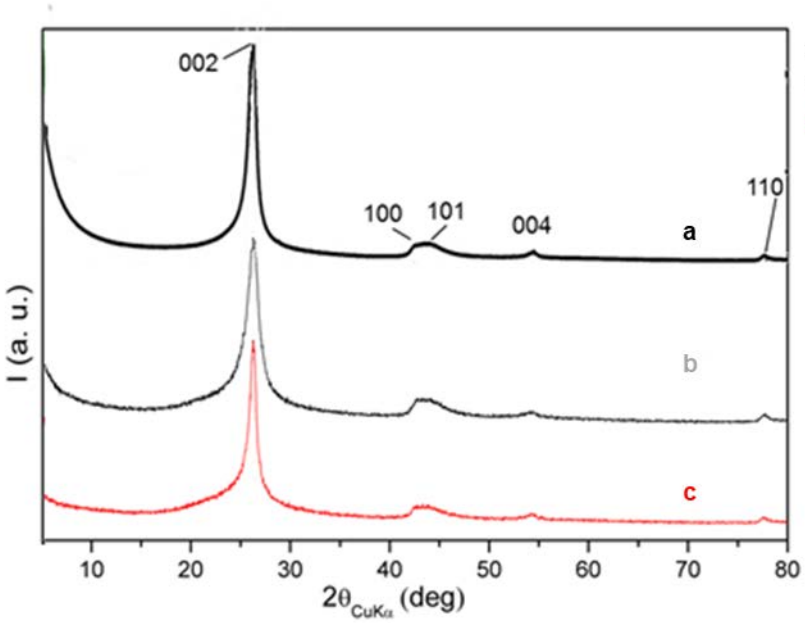
➢ IR findings support the formation of HSAG/Pyr adduct

Sample	I_D/I_G
HSAG	1.21
HSAG T	1.19
HSAG/PyrEst T	1.47
HSAG M	1.58
HSAG/PyrEst M	1.83



➢ Substantially unaltered bulk structure

Characterization of Adducts – WAXD



a) HSAG
b) HSAG/Pyr-COOEt-M
c) HSAG/Pyr-COOEt-T 160°C

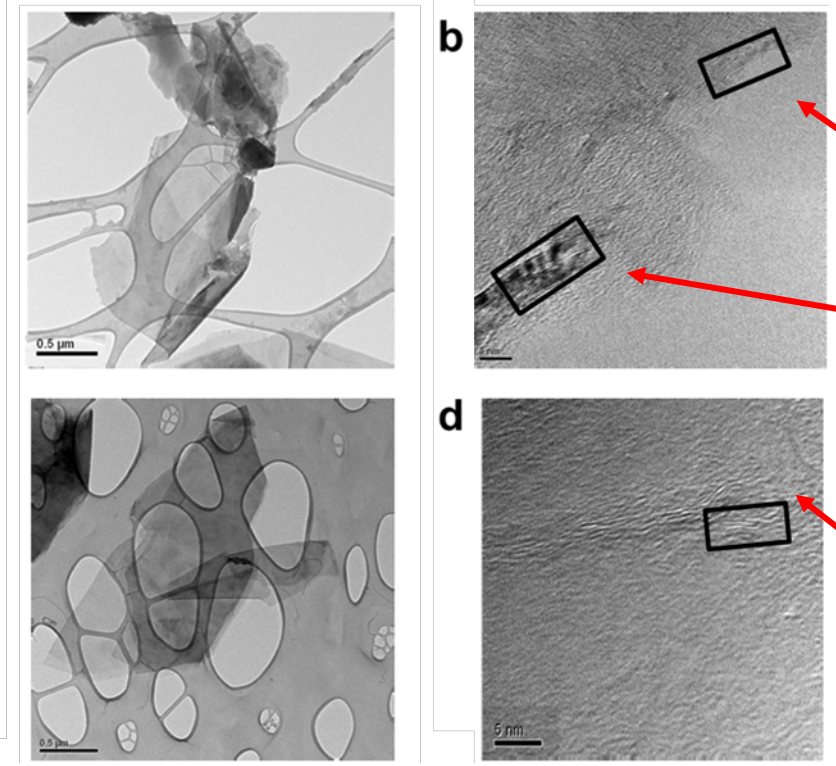
Sample	number of layers
HSAG	35
HSAG-P/M	21
HSAG-P/T 160°C	31

- No expansion of the interlayer distance
- Unaltered in plane order

- Edge (peripheral) functionalization of graphene layers

Characterization of Adducts – HRTEM

HSAG-P/T 160°C adduct



9 layers

20 layers

3-4 layers

Water suspension

Sonication

Centrifugation 6000 rpm, 30 min

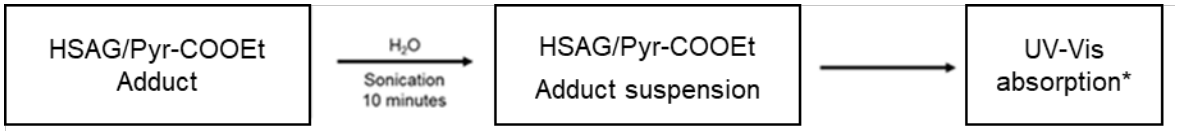
Supernatant

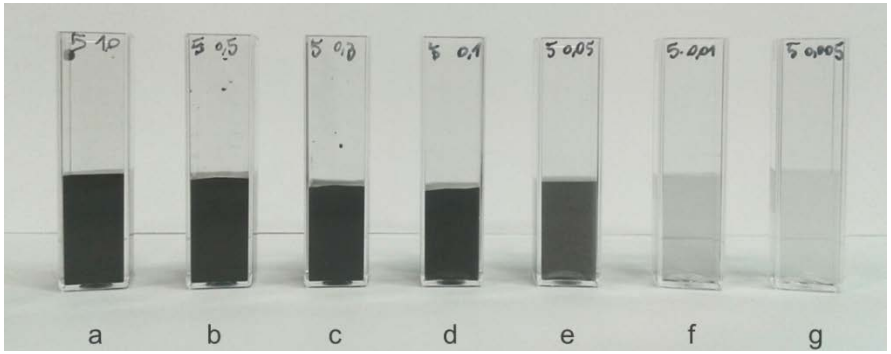
After drop deposition

HSAG-P/M adduct

➢ Exfoliation to few layers graphene

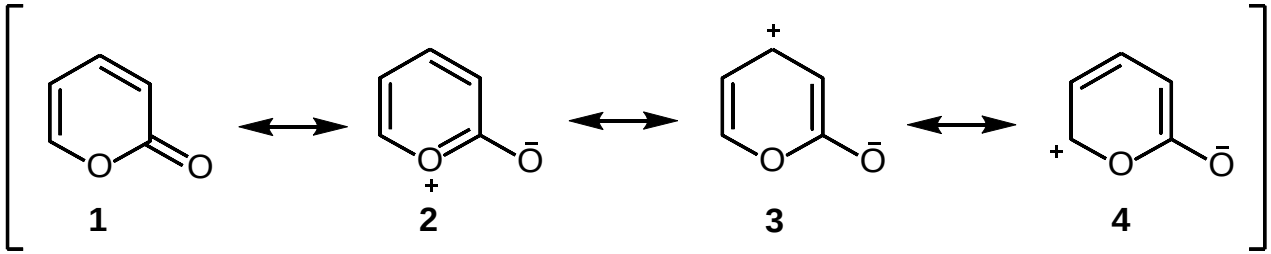
Water suspensions of HSAG adducts with PyrEst



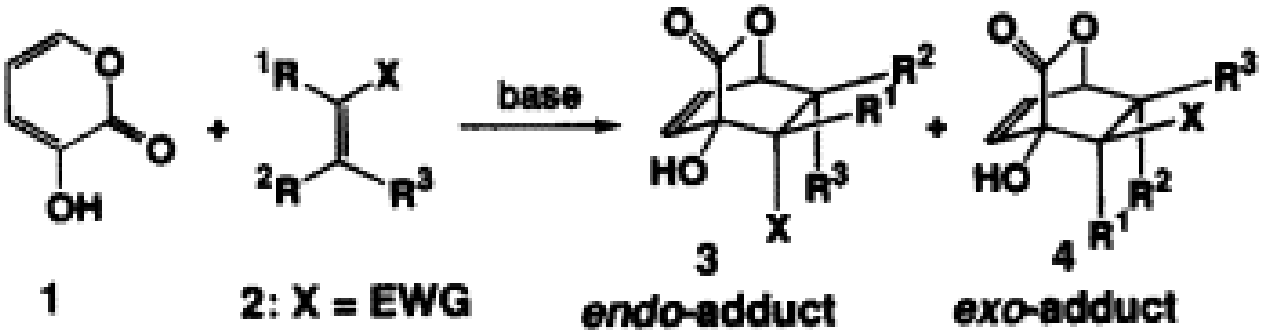


- Stable water suspension, even after 1 week

What about the mechanism?



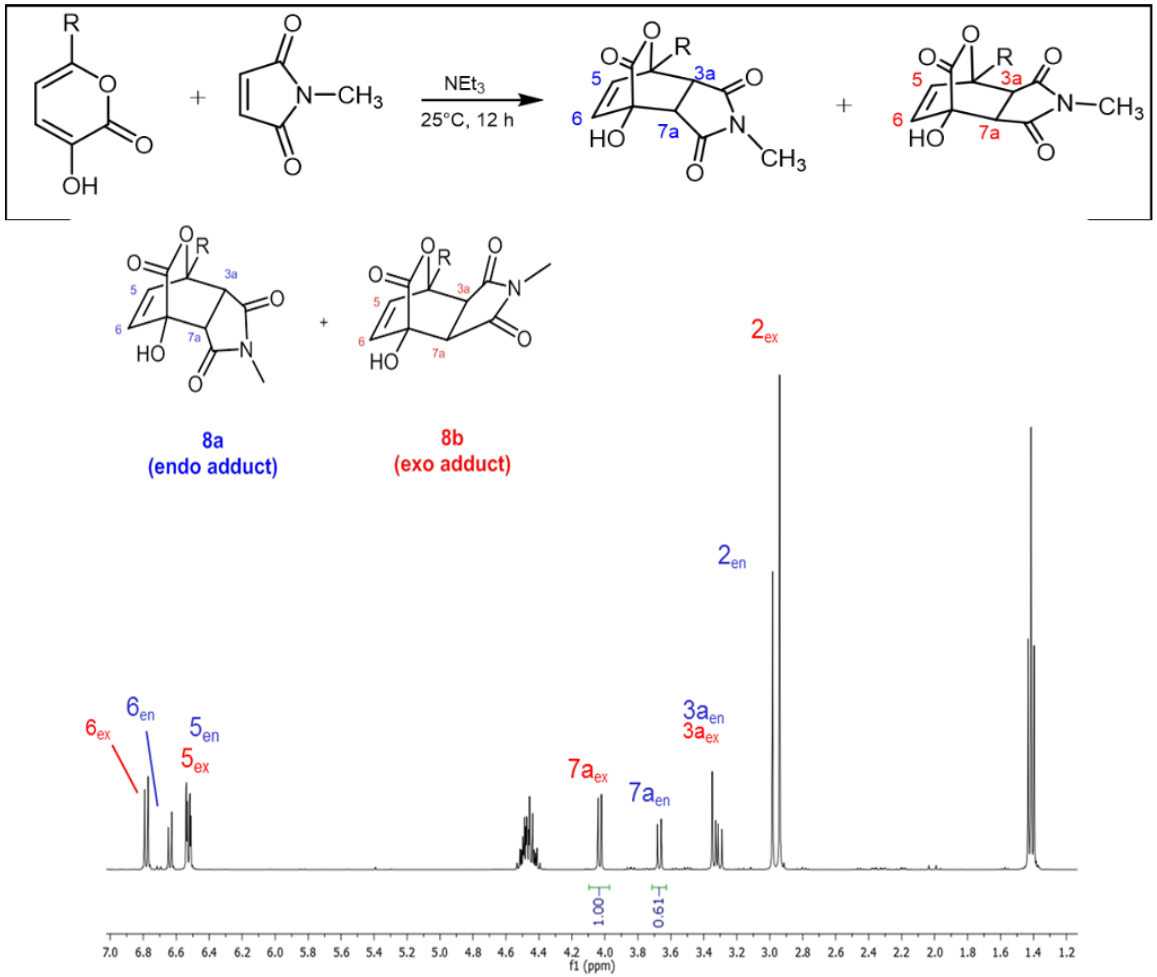
2-pyrone is able to act as diene in Diels Alder reactions



Okamura, H., Iwagawa, T., & Nakatani, M. (1995). *Tetrahedron letters*, *36*(33), 5939-5942.

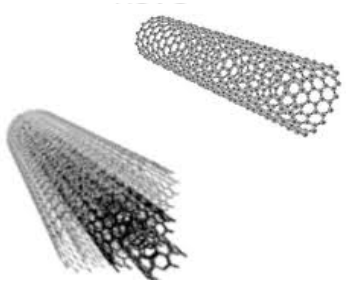
Pyrone compounds as functionalizing molecules for sp^2 carbon allotropes

Model reaction: 5-hydroxy-6-oxo-6*H*-pyran-2-carboxylic acid ethyl ester (Pyr-Est) with a dienophile such as *N*-methylmaleimide



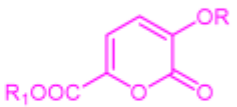
F.Margani, M. Magrograssi, M. Piccini, L. Brambilla, V.Barbera, M. Galimberti, – ACS Sustainable Chemistry & Engineering 10, no. 13 (2022): 4082-4093.

Carbon allotropes functionalization



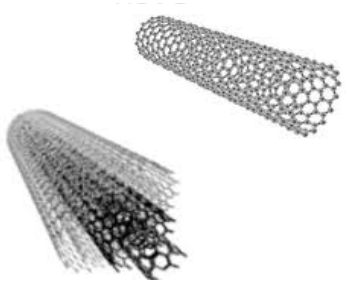
+

Pyrones
(P)



Main objective

To introduce oxygenated functional groups on HSAG, CNT and CB without altering the bulk crystalline structure of the graphitic substrate



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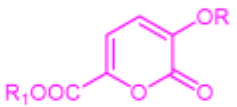
Pyrones
(P)



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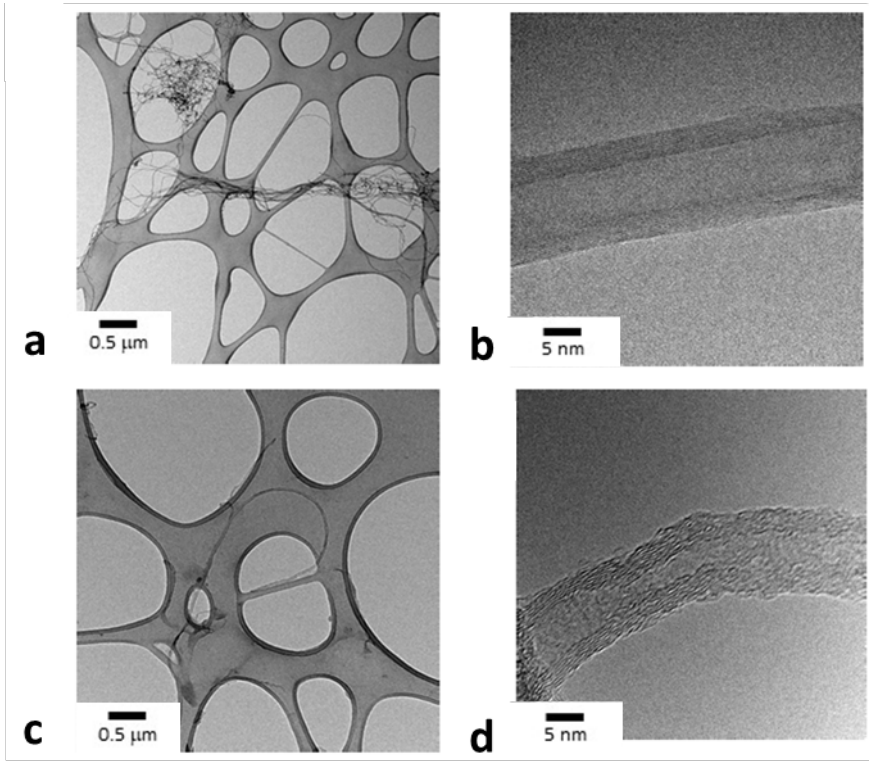


Pristine CNTs

CNTs/Pyr

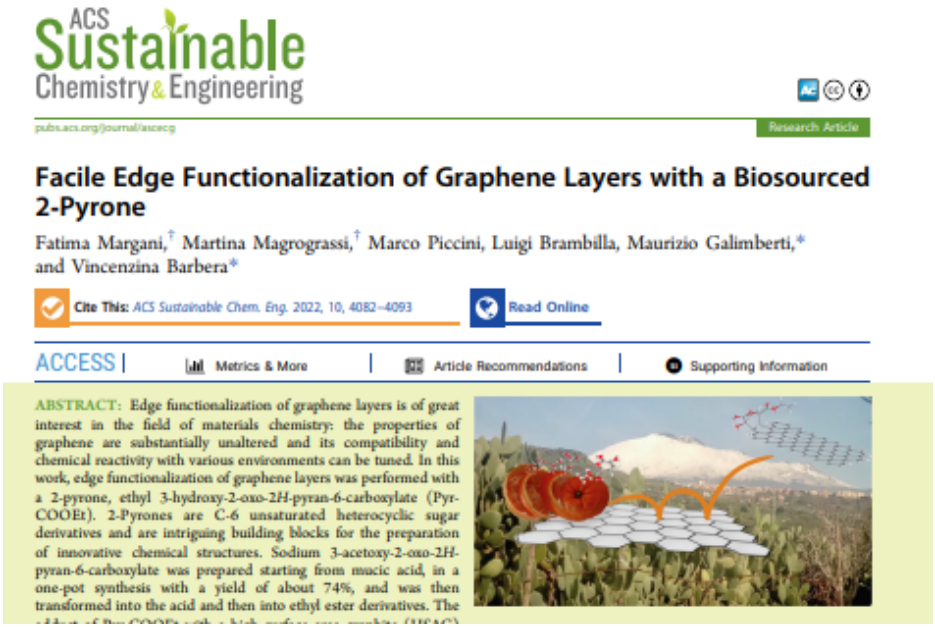
M. Magrograssi – Master Thesis, Politecnico di Milano, 2018.

Preparation of Adducts of Pyrone with HSAG - Resume

- Introduction of oxygenated functional group onto the carbon allotropes
- Very high yield of the modification, even about 91%
- Egde (peripheral) functionalization of graphene layers
- Exfoliation in water suspension
- Stable water dispersion

Bio-Edge GO

Versatile platform for the preparation of further derivatives



ACS Sustainable Chemistry & Engineering

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Research Article

Facile Edge Functionalization of Graphene Layers with a Biosourced 2-Pyrone

Fatima Margani,† Martina Magrograssi,† Marco Piccini, Luigi Brambilla, Maurizio Galimberti,* and Vincenzina Barbera*

Cite This: ACS Sustainable Chem. Eng. 2022, 10, 4082−4093 | Read Online

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ABSTRACT: Edge functionalization of graphene layers is of great interest in the field of materials chemistry: the properties of graphene are substantially unaltered and its compatibility and chemical reactivity with various environments can be tuned. In this work, edge functionalization of graphene layers was performed with a 2-pyrone, ethyl 3-hydroxy-2-oxo-2*H*-pyran-6-carboxylate (Pyr-COOEt). 2-Pyrones are C-6 unsaturated heterocyclic sugar derivatives and are intriguing building blocks for the preparation of innovative chemical structures. Sodium 3-acetoxy-2-oxo-2*H*-pyran-6-carboxylate was prepared starting from mucic acid, in a one-pot synthesis with a yield of about 74%, and was then transformed into the acid and then into ethyl ester derivatives. The

Innovative Sustainable Materials Group

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Thanks for your attention!

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PhD thesis financed by Pirelli Tyre