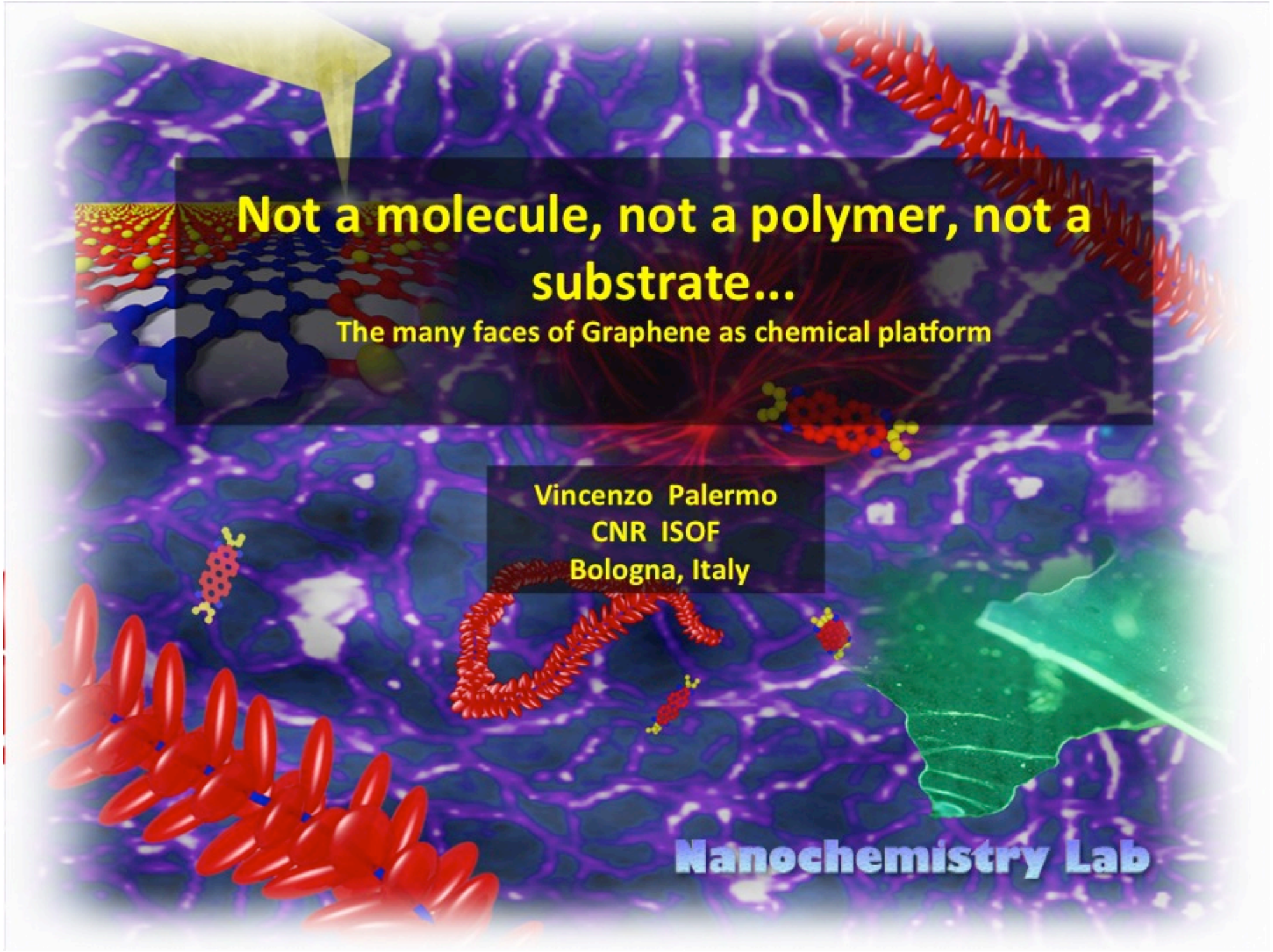
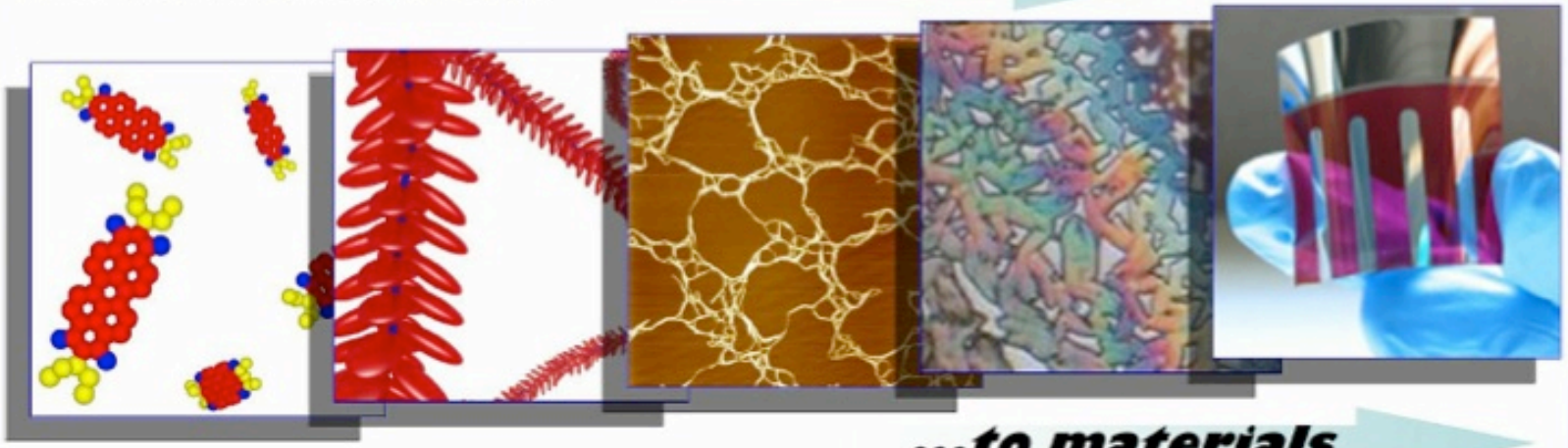

Not a molecule, not a polymer, not a substrate...
The many faces of Graphene as chemical platform
Vincenzo Palermo
CNR ISOF
Bologna, Italy
Nanochemistry Lab

CNR – INSTITUTE FOR ORGANIC SYNTHESIS AND PHOTOREACTIVITY

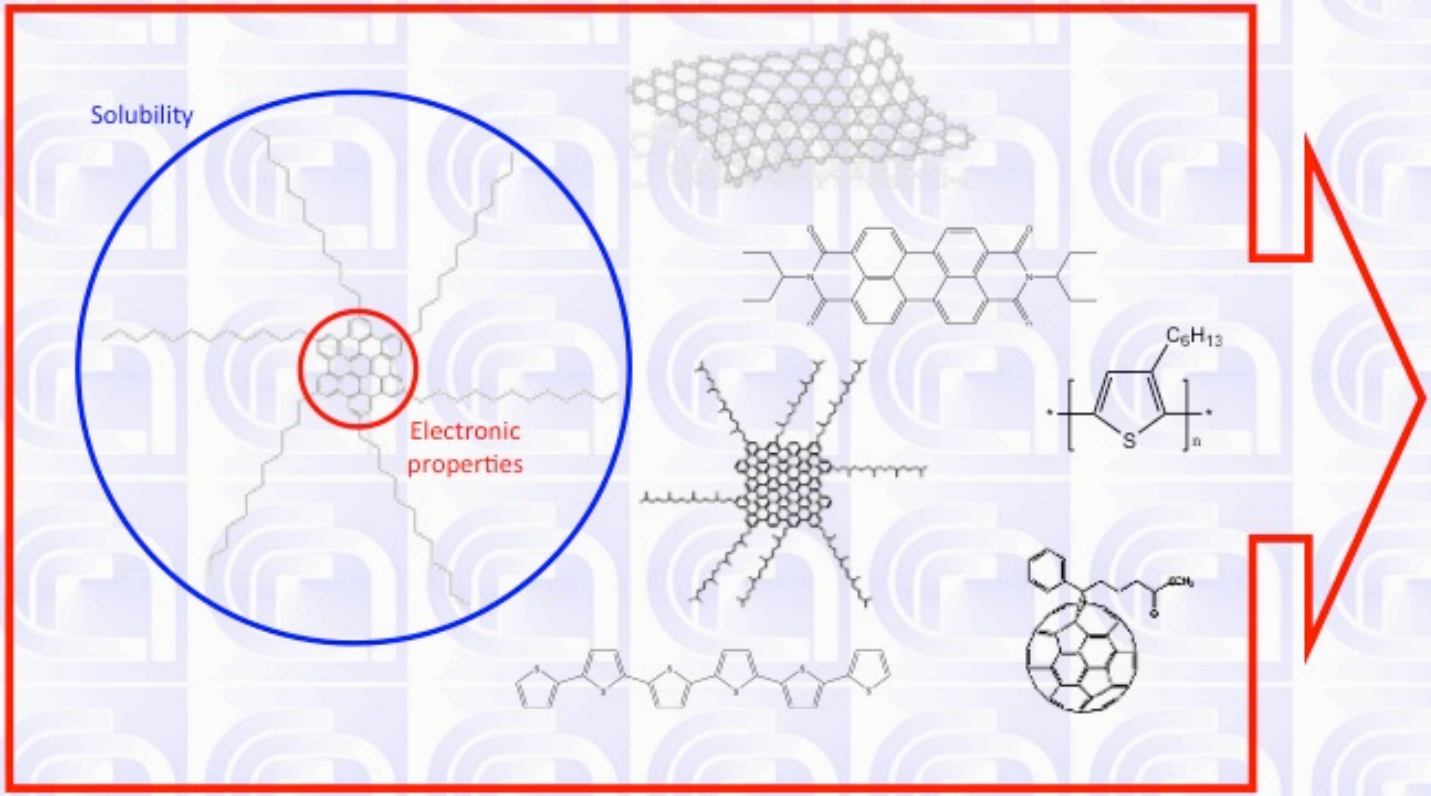
From molecules...



...to materials

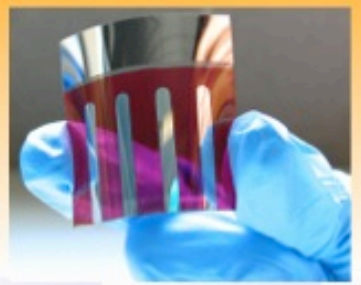
Nanochemistry Lab

Functional organic materials



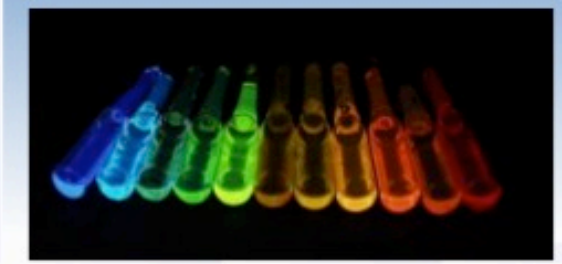
Main applications in the fields of:

Photovoltaics



Microelectronics

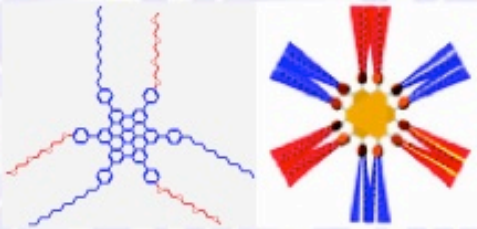
Bio-diagnostics



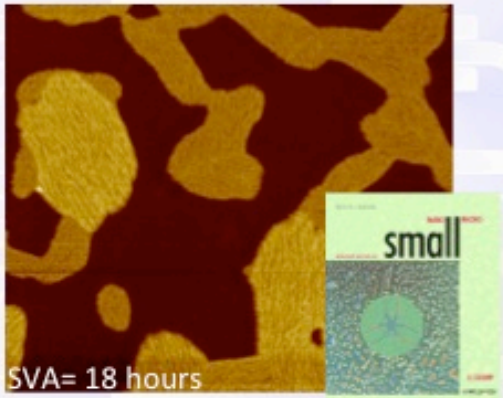
Nanochemistry Lab

SELF-ASSEMBLY FROM NANO- TO MACRO-SCALE

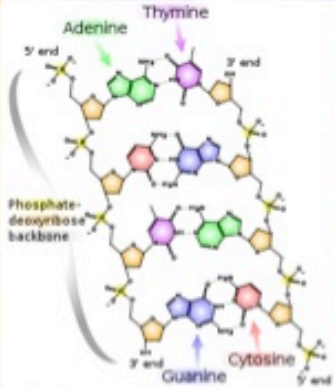
HYDROPHOBIC- HYDROPHILIC INTERACTIONS

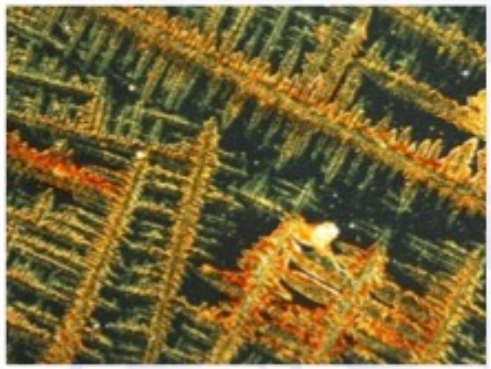


CORONENES



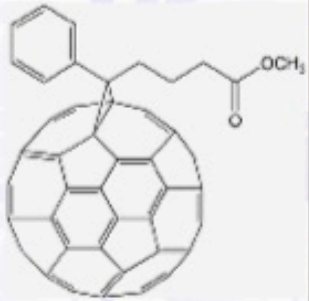
HYDROGEN BONDING



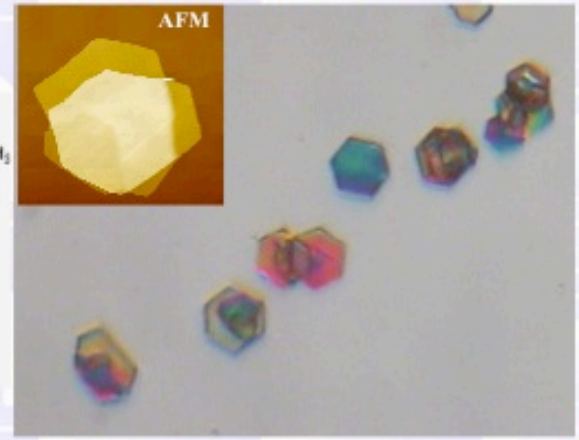


NUCLEOBASES

NEW DEPOSITION TECHNIQUES



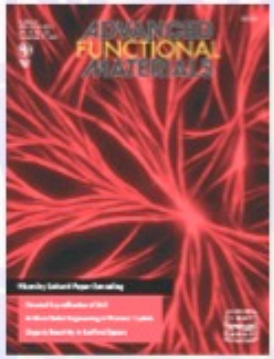
FULLERENES

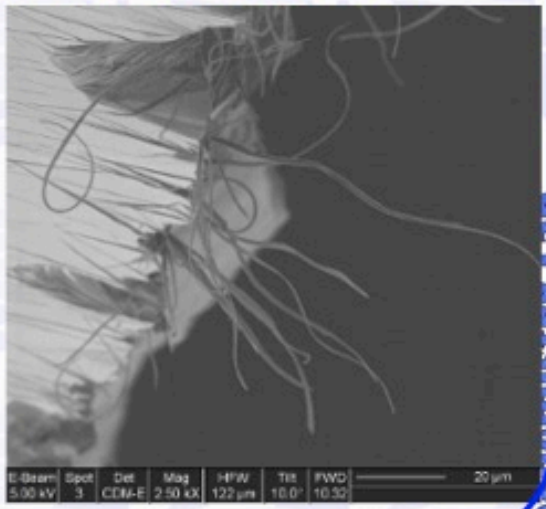


150 x 125 µm

POST-PROCESSING TECHNIQUES

PERYLENES





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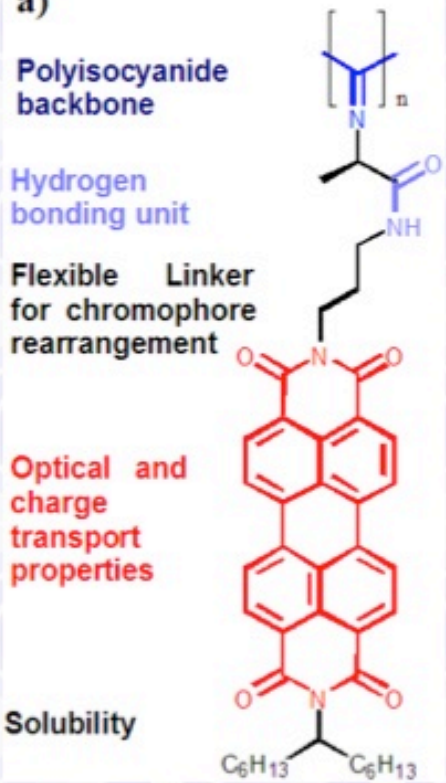
Advanced Functional Materials, (2007) **17**, 3791.
Journal of Materials Chemistry, (2010) **20**, 71.
Soft Matter, (2008) **4**, 2064.
Carbon, (2012) **50**, 1332.

Advanced Functional Materials, (2011) **21**, 1279.
Journal of Materials Chemistry, (2010) **20**, 2493.
Macromolecular Rapid Communications, (2010) **31**, 351.
Small, (2009) **5**, 112

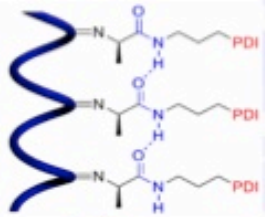
TAKING THE BEST OF TWO MATERIALS

COVALENT STRUCTURE OF THE BUILDING BLOCK

a)

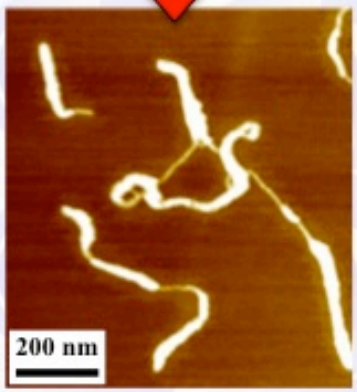


HYDROGEN BONDING

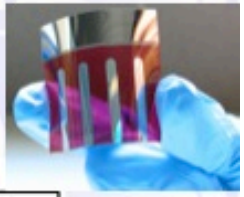


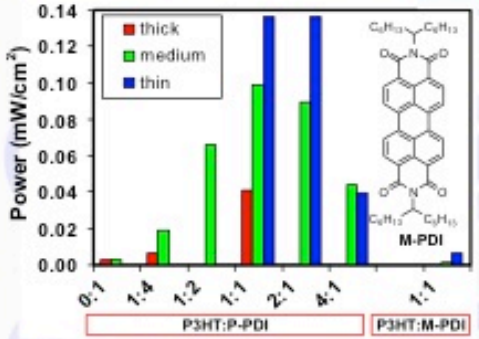
COILING

SUPER-COILING

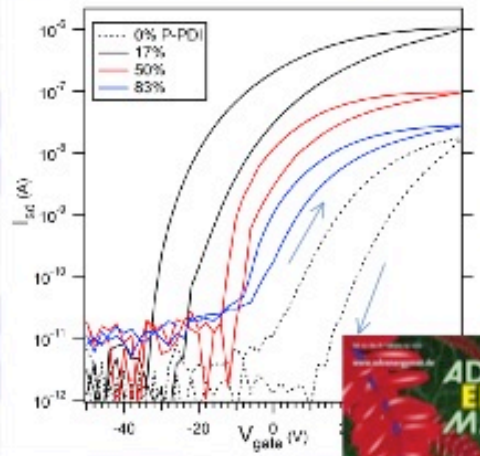


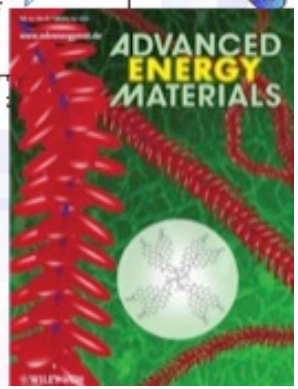
BETTER EFFICIENCY THAN MONOMER AND POLYMERS IN PHOTOVOLTAICS...





...AND TRANSISTORS

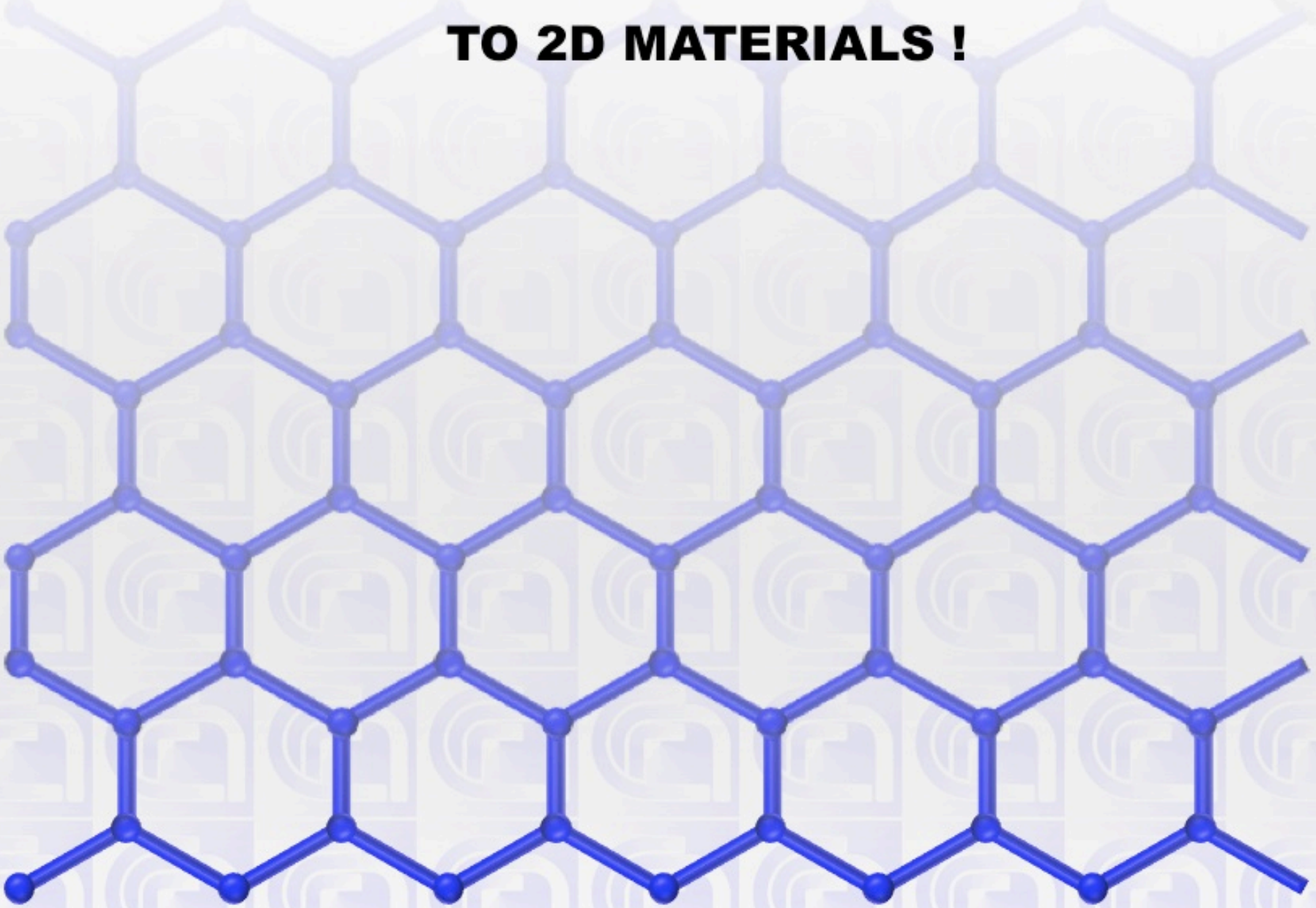




Advanced Materials, (2010) 22, E81.
Journal of the American Chemical Society, (2009) **131**, 7055.
Advanced Functional Materials, (2008) **18**, 3947.
Journal of the American Chemical Society, (2008) **130**, 14605.
Soft Matter, (2009) **5**, 4680.
Chemistry of Materials, (2010) **22**, 2597.
Chemistry-a European Journal, (2009) **15**, 2536.

PARADIGM SHIFT: FROM 1D POLYMERS...

TO 2D MATERIALS !



Nanochemistry Lab

ChemComm

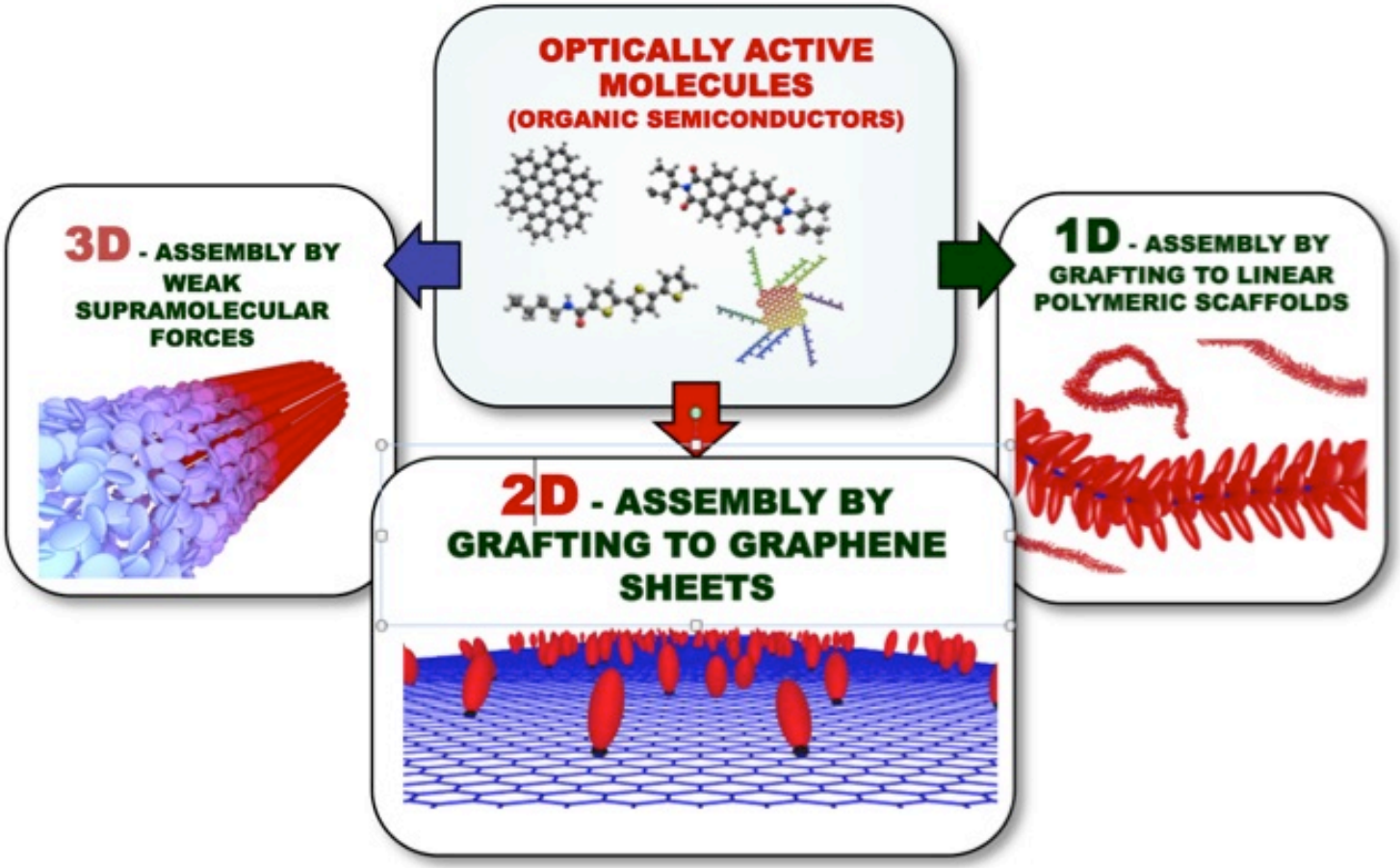
RSC Publishing

FEATURE ARTICLE

Not a molecule, not a polymer, not a substrate... the many faces of graphene as a chemical platform

Cite this: Chem. Commun., 2013, 49, 2848

Vincenzo Palermo*



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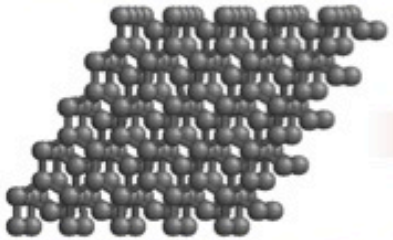
V. PALERMO, *Chem. Commun.*, 2013, **49**, 2848

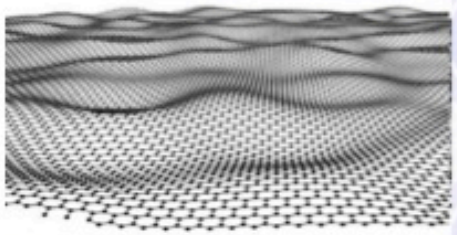
GRAPHENE RESEARCH @ ISOF

GRAPHITE



GRAPHENE

(NEWEST AND MOST STUDIED CARBON-BASED MATERIAL)



APPLICATIONS

TRANSPARENT CONDUCTING DISPLAYS
(ITO replacement)

ELECTRON ACCEPTOR
(excellent charge mobility, very high surface area)

COATINGS
(inert, high barrier to oxygen and moisture)

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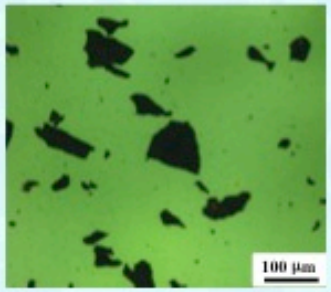
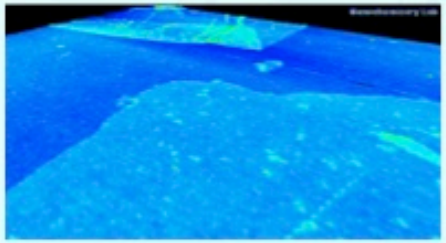
GRAPHENE PRODUCTION AND RESEARCH @CNR Bologna

SOLUTIONS
in water and solvents, gram scale



MONOATOMIC SHEETS
Size from 1 to 100 µm



COATINGS
on silicon, glass, quarz, metals…

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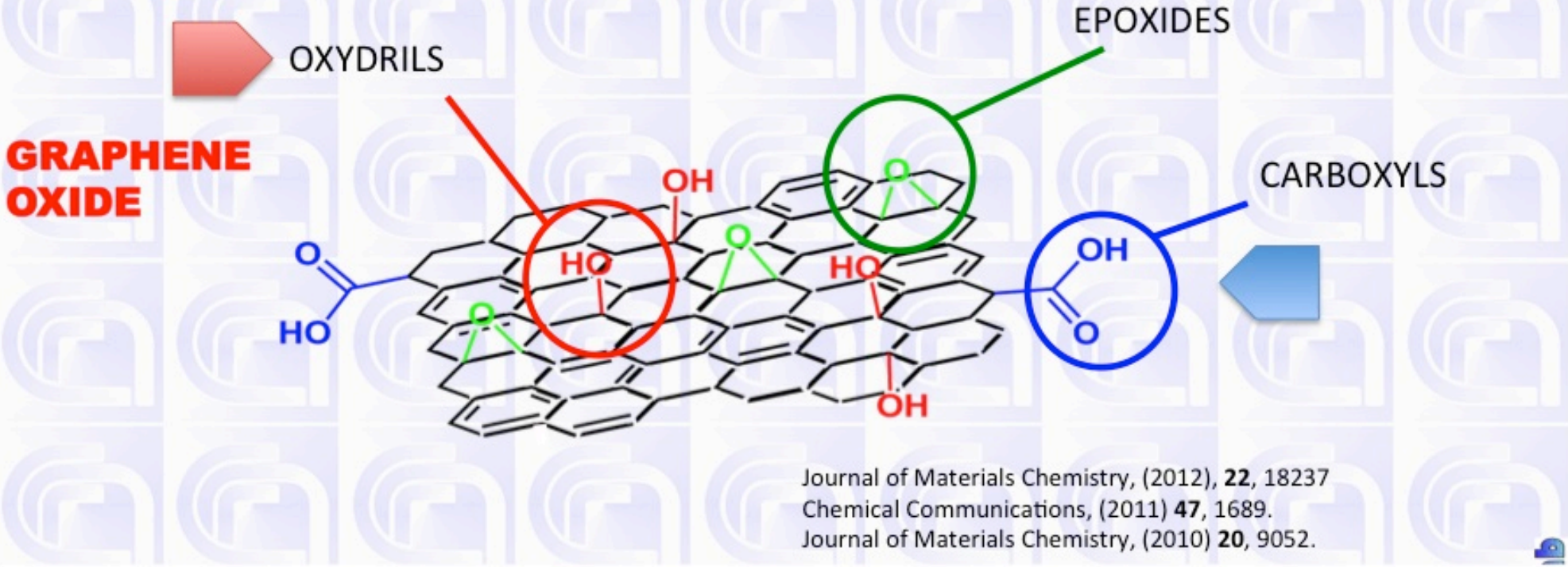
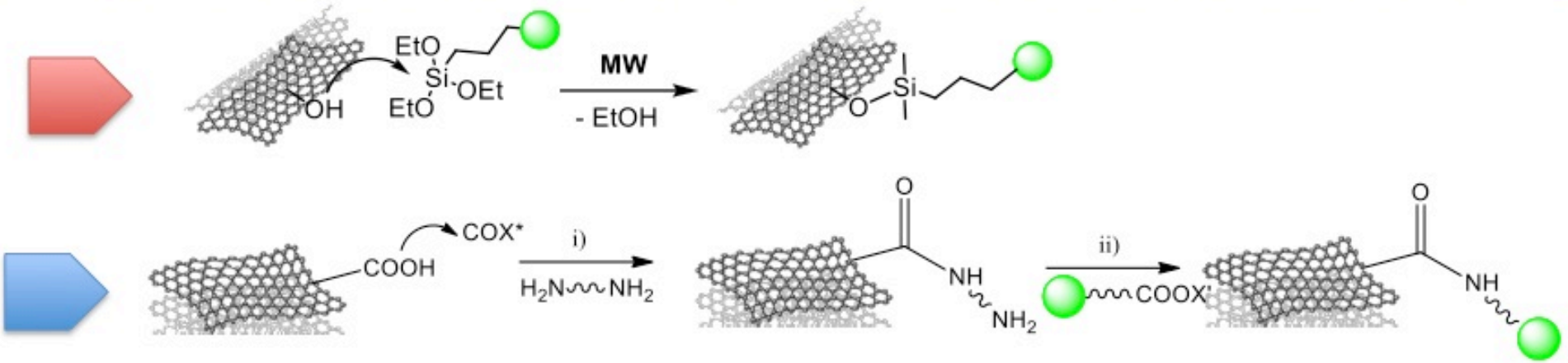
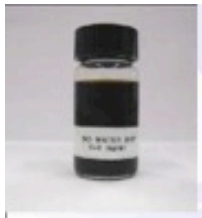
GRAPHENE AS A MOLECULE

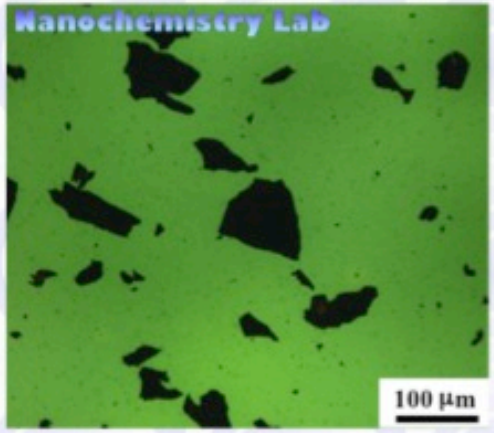


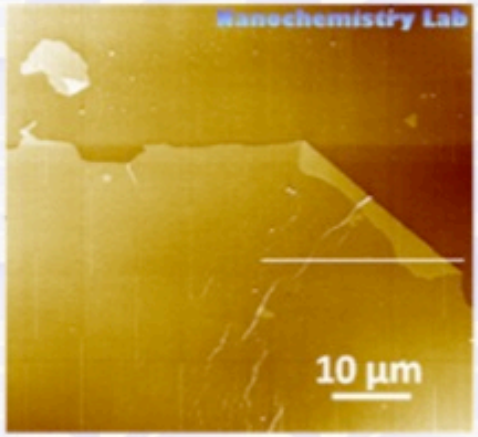
Journal of Materials Chemistry, (2012), **22**, 18237
Chemical Communications, (2011) **47**, 1689.
Journal of Materials Chemistry, (2010) **20**, 9052.

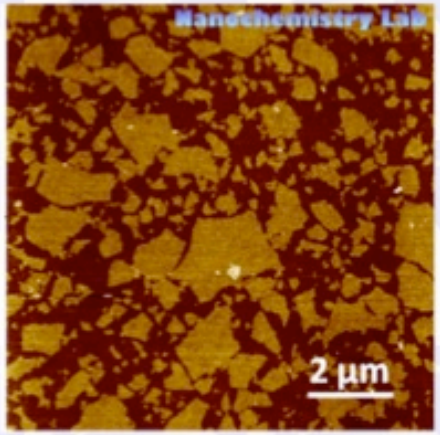


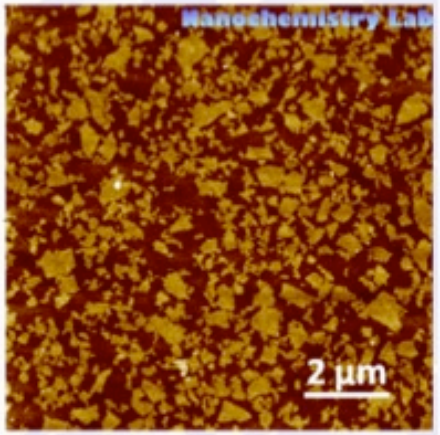


GRAPHENE OXIDE:
Size control on 2 orders of magnitude (1-100 um)

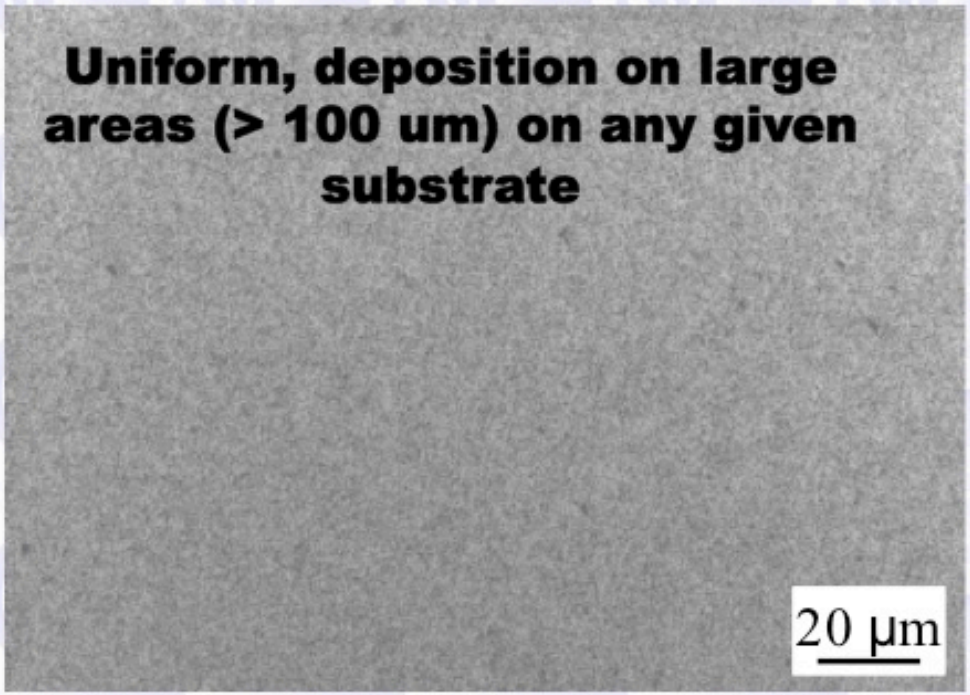




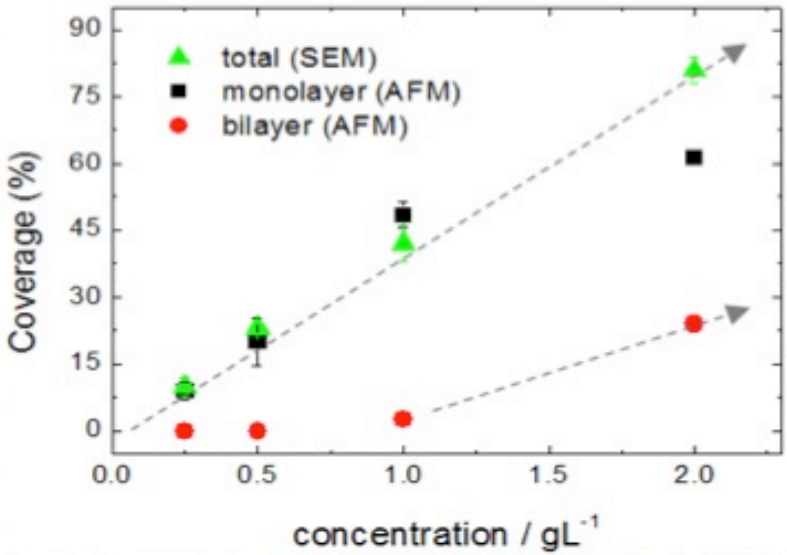




Uniform, deposition on large areas (> 100 um) on any given substrate



Coverage evolution

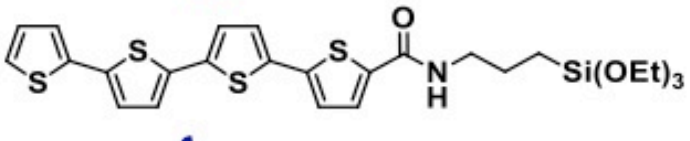


J. Mater. Chem., 2011, **21**, 2924

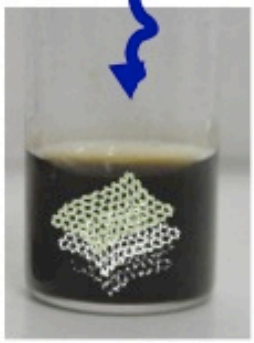
Nanochemistry Lab

COVALENT GRAFTING OF OPTICALLY ACTIVE MOLECULES BY DIRECT MW ASSISTED SYLYLATION OF GO

T4



GO



MW

100 W, 80°C,
40 min, DMF

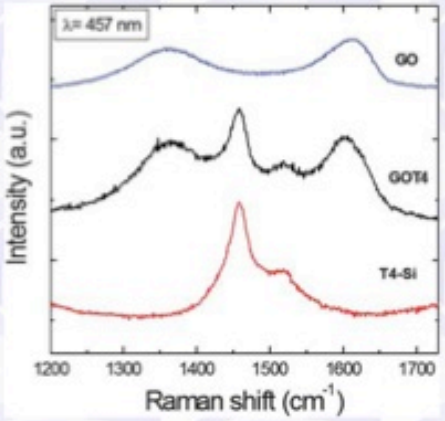
GOT4

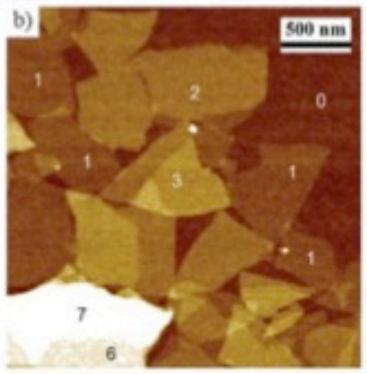
functionalization loading ≈2.6 %

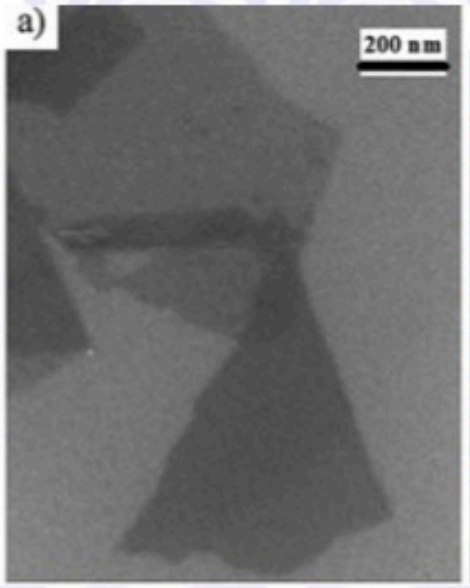
Journal of Materials Chemistry, (2010) **20**, 9052.

Facile covalent functionalization of graphene oxide using microwaves: bottom-up development of functional graphitic materials†

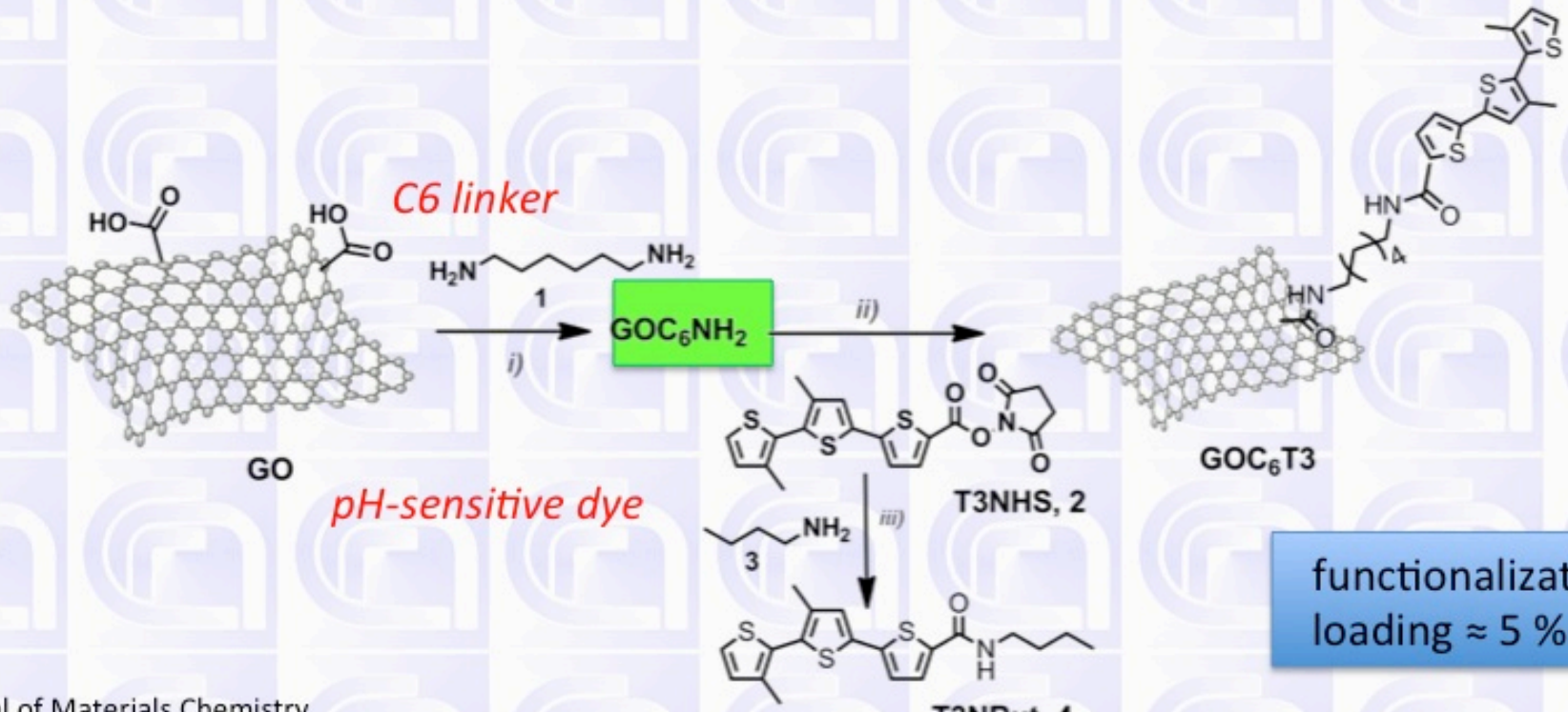
Manuela Melucci,[*ab] Emanuele Treossi,[a] Luca Ortolani,[c] Giuliano Giambastiani,[b] Vittorio Morandi,[c] Philipp Klar,[d] Cinzia Casiraghi,[d] Paolo Samorì[ae] and Vincenzo Palermo[*a]





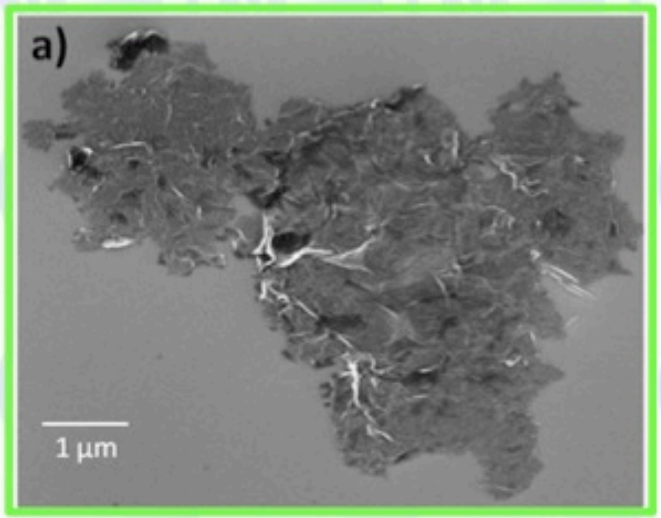


SUBSTITUTION OF ACTIVATED GO-COOH



functionalization
loading ≈ 5 %

Journal of Materials Chemistry, (2012), **22**, 18237

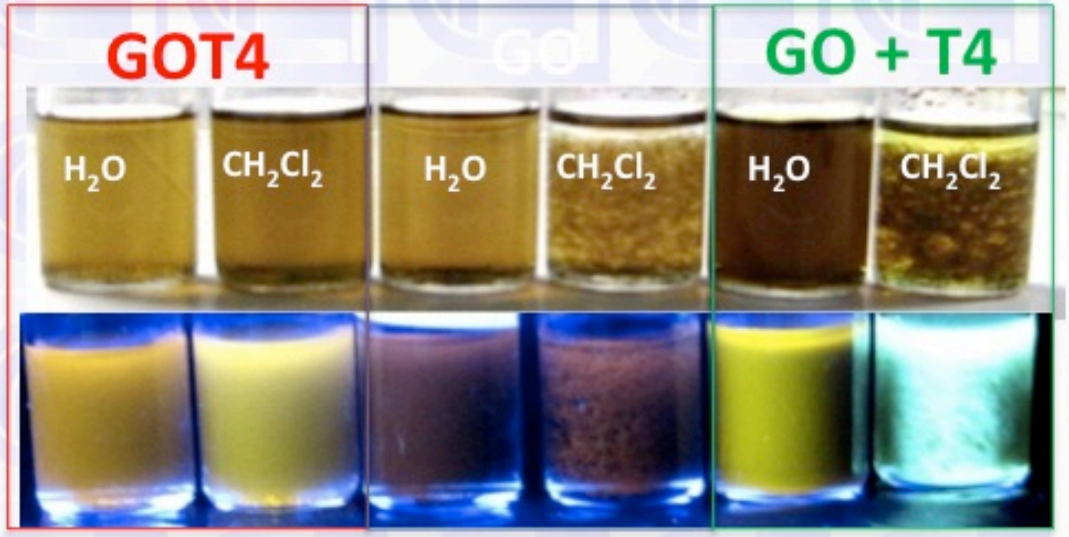


Graphene–organic hybrids as processable, tunable platforms for pH-dependent photoemission, obtained by a new modular approach†

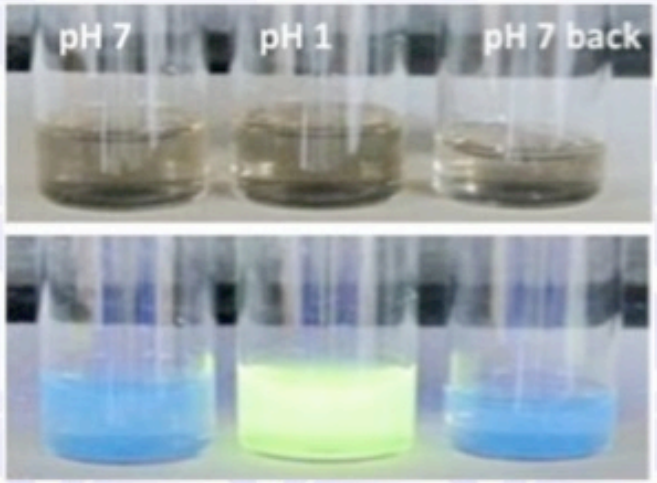
Manuela Melucci,‡*ab Margherita Durso,‡a Massimo Zambianchi,‡a Emanuele Treossi,§ac Zhen-Yuan Xia,§a Ilse Manet,¶a Giuliano Giambastiani,‖b Luca Ortolani,**c Vittorio Morandi,**c Filippo De Angelis††d and Vincenzo Palermo§*a

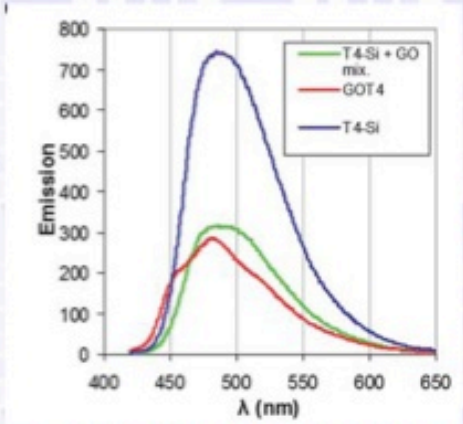
New solubility/optical and responsive properties of graphene-organic hybrids

GOT4 – improved solubility



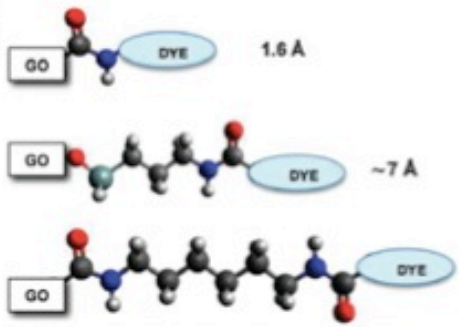
GOT3: pH induced fluorescence switch

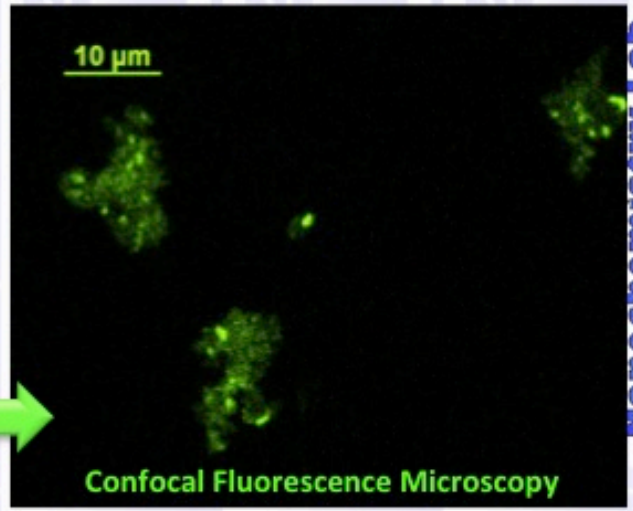




FLUORESCENCE QUENCHING

DIFFERENT LINKERS INFLUENCE INTERACTION BETWEEN GRAPHENE AND DYE





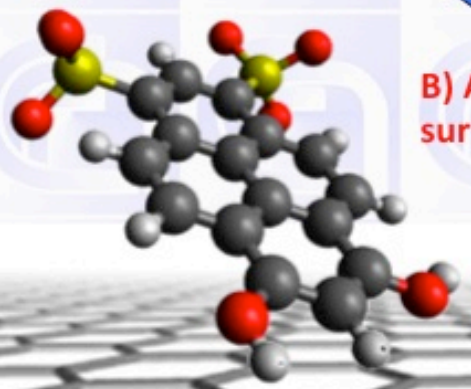
Nanochemistry Lab

GRAPHENE AS A SUBSTRATE

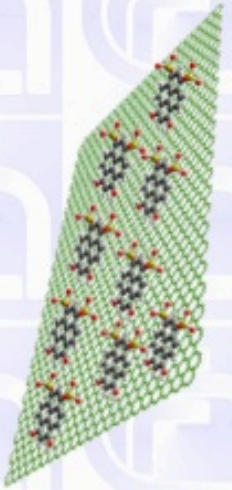
Steps involved in graphite exfoliation

A) Solubility and self-assembly of each dye in solution (not discussed here)

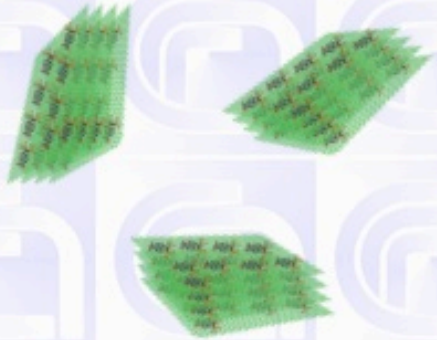
B) Adsorption of dye on graphite surface



C) Exfoliation of GRAPHENE in solution

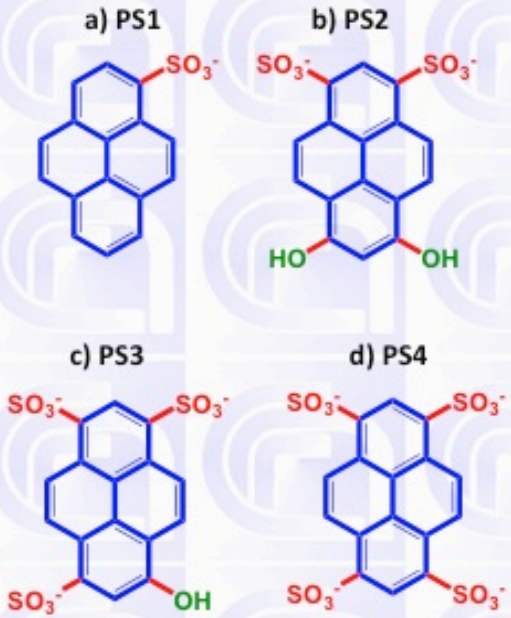


D) (Eventual) re-aggregation of the sheets in solution



Nanoscale, **5**, 4205 (2013).

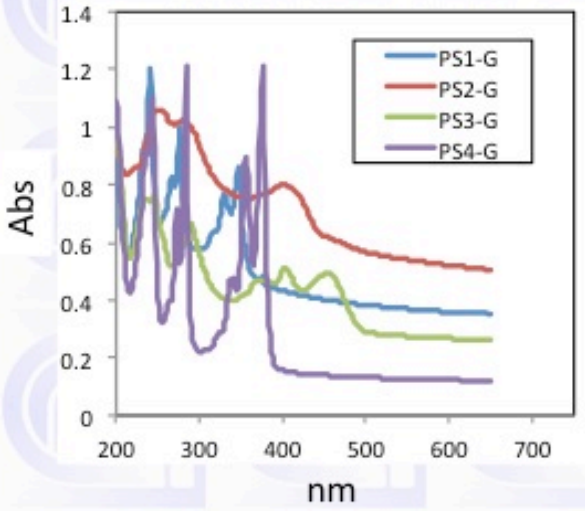
MONITORING EXFOLIATION WITH OPTICAL SPECTROSCOPY

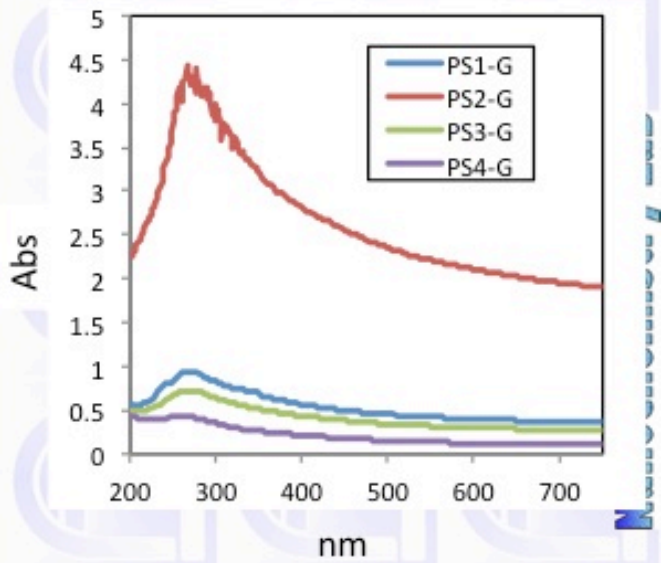


SONICATION OF GRAPHITE IN AN EXCESS OF DYE

DYE EXCESS REMOVAL
+
AGGREGATES
REMOVAL

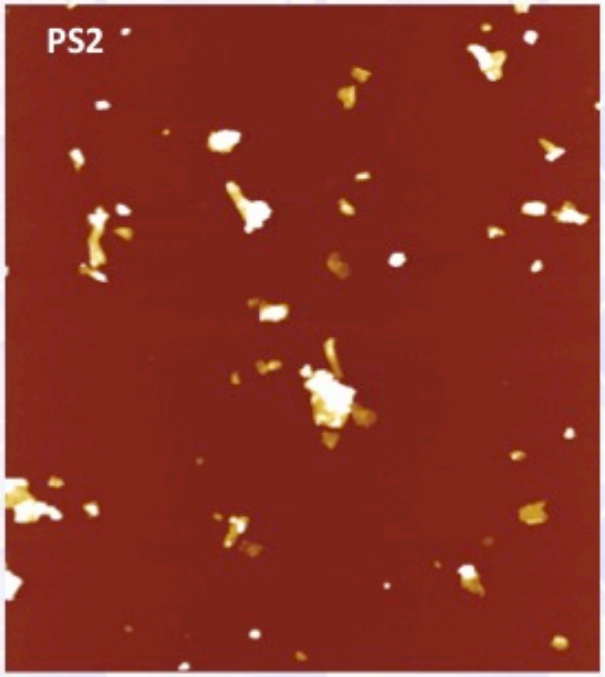
MONITORING EXFOLIATION PROCESS BY OPTICAL SPECTROSCOPY

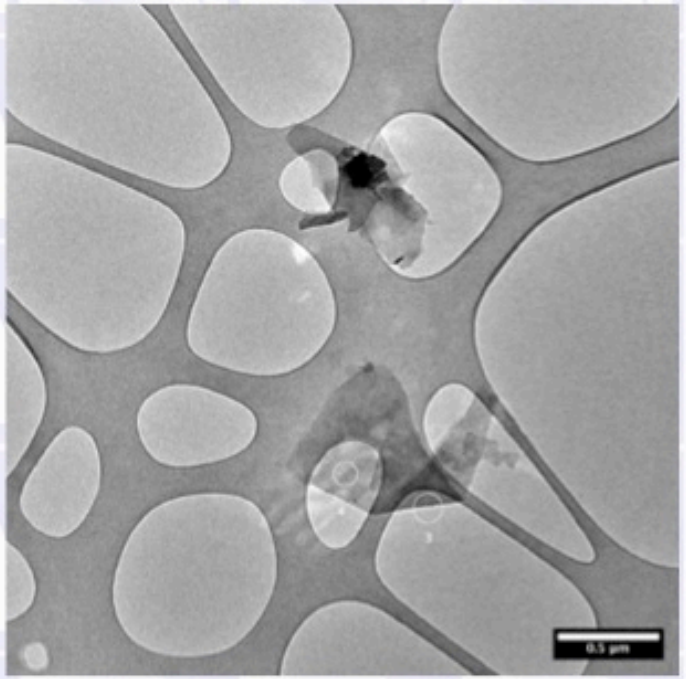


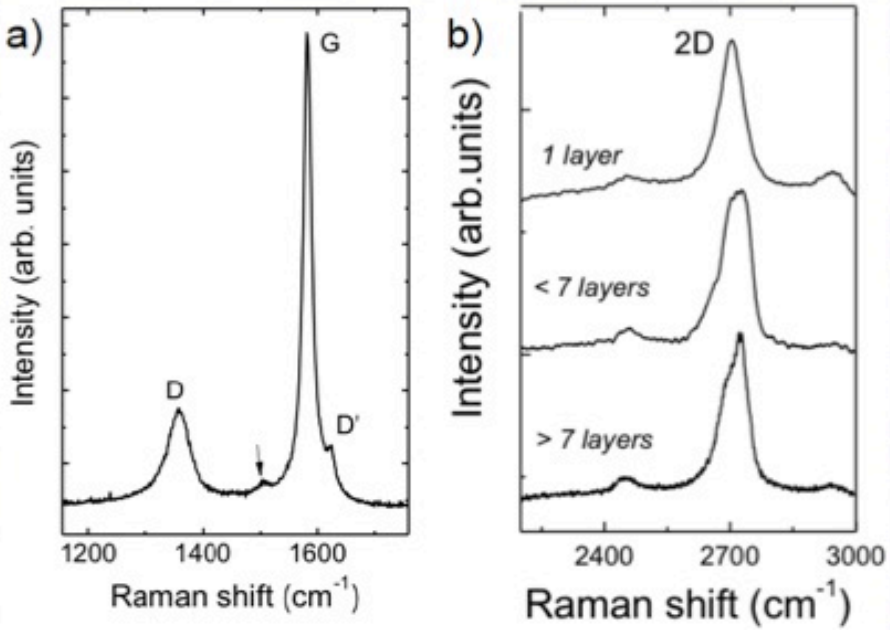


Nanoscale, **5**, 4205 (2013).

NANOSCALE CHARACTERIZATION







Molecule	% single layers	% thin sheets (2-7 layers)	% thick sheets (>7 layers)	Total
PS1	18	68	14	100
PS2	15	55	31	100
PS3	22	65	13	100
PS4	9	55	36	100

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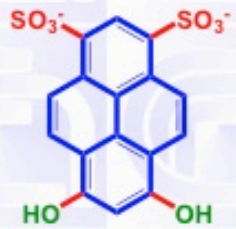
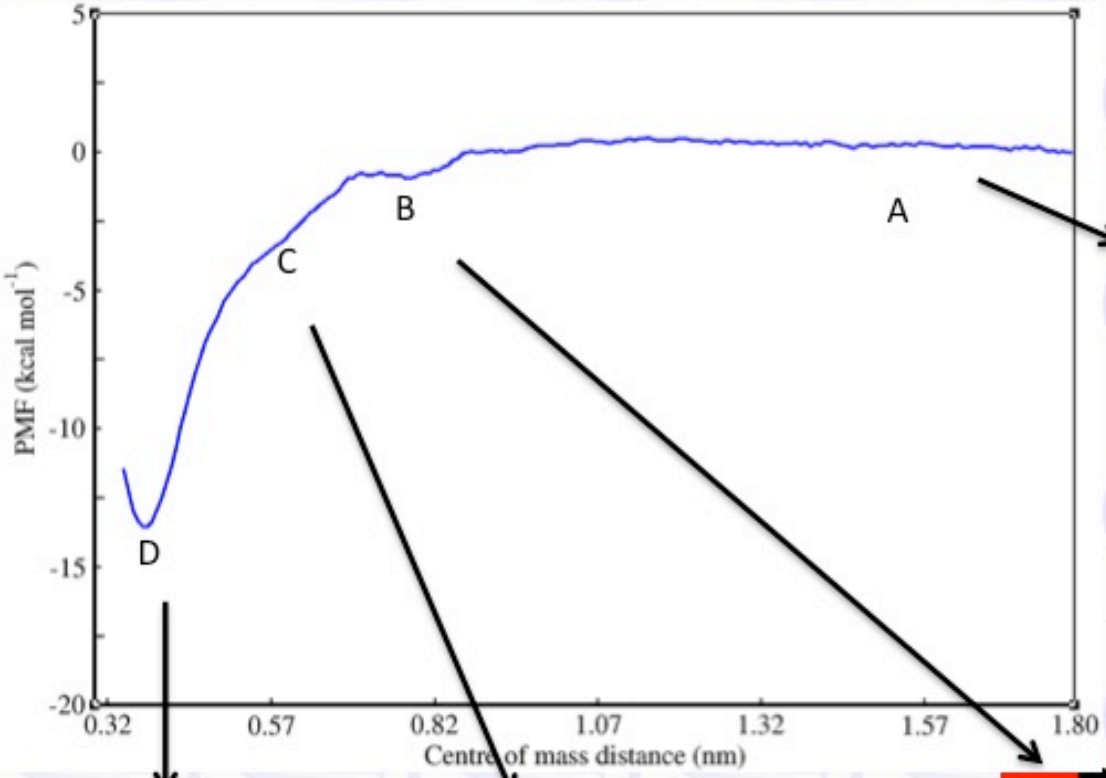
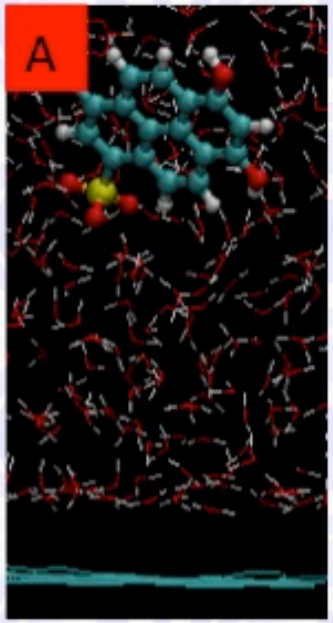
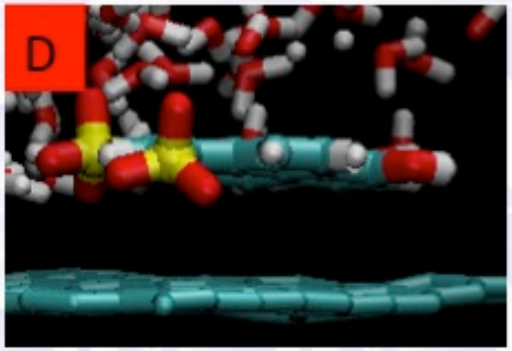
MODELLING OF PS2 INTERACTION WITH GRAPHENE

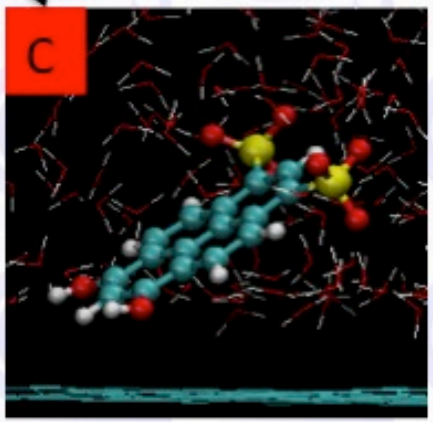
PS2

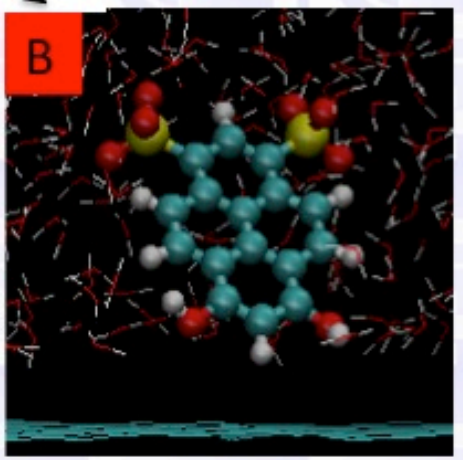












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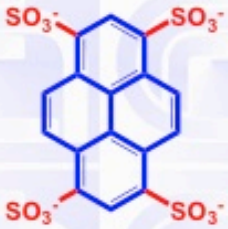
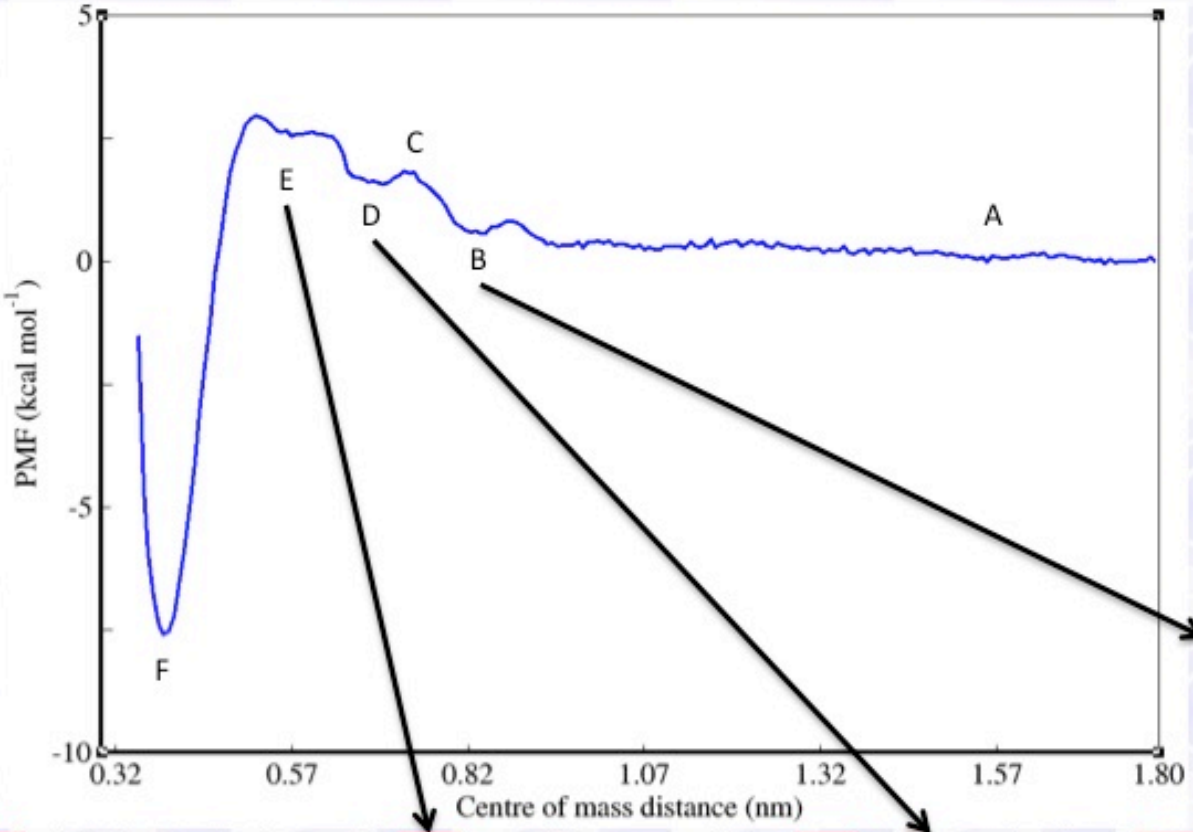
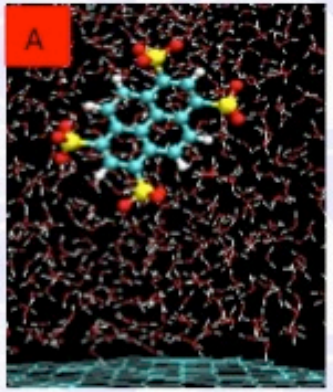
Nanoscale, **5**, 4205 (2013).

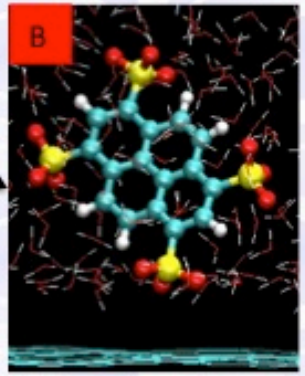
MODELLING OF PS4 INTERACTION WITH GRAPHENE

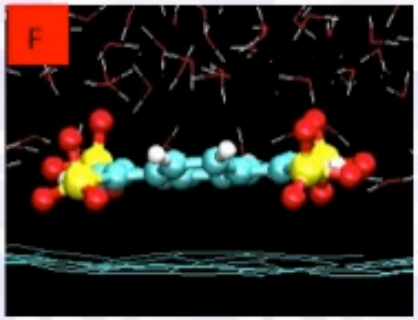
PS4

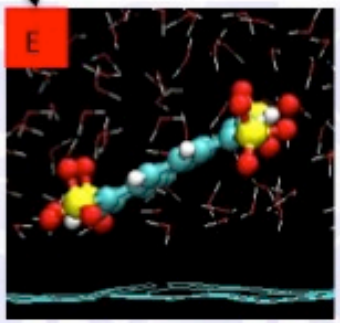


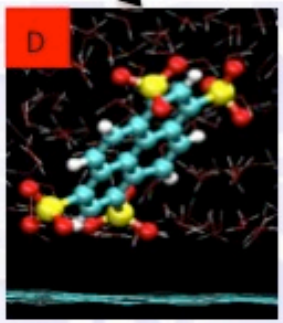


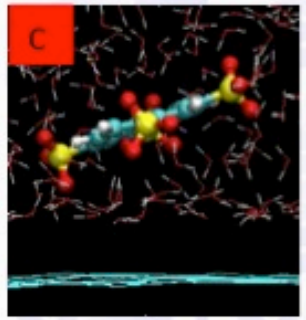












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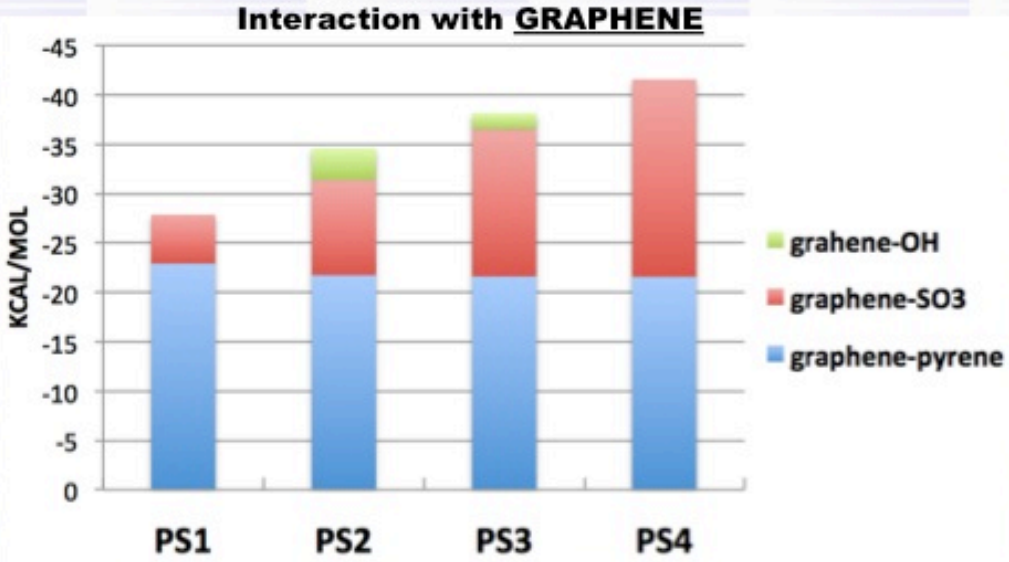
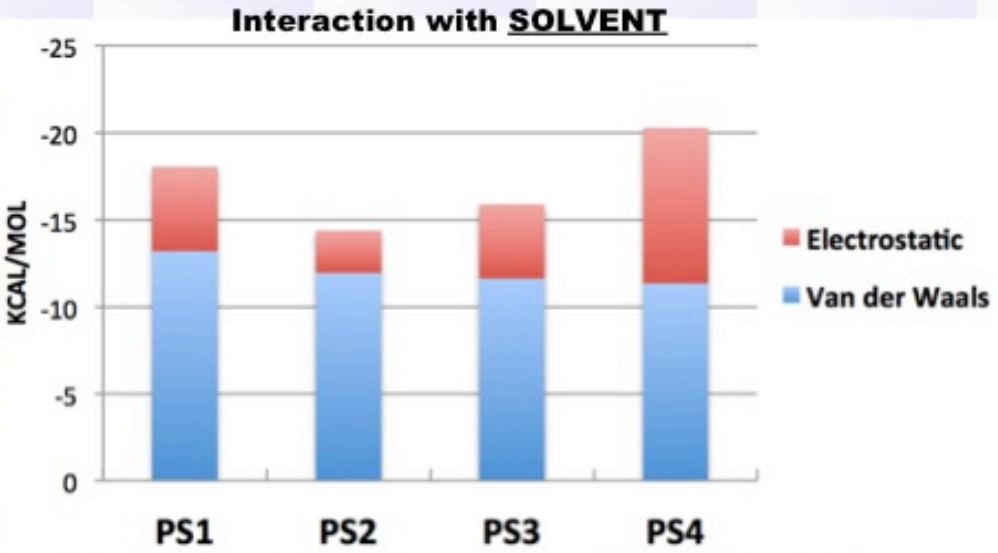
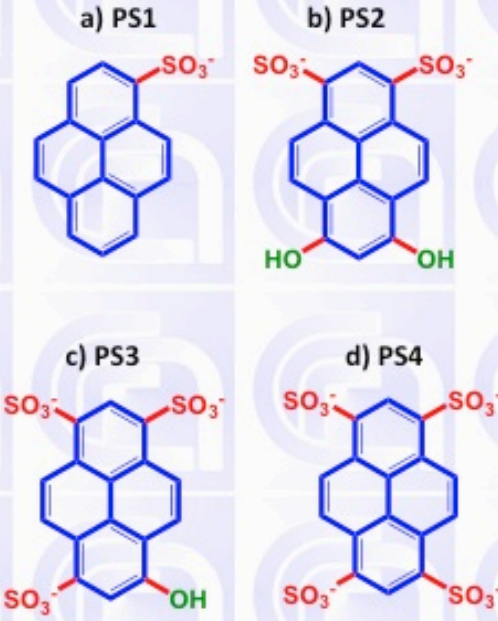
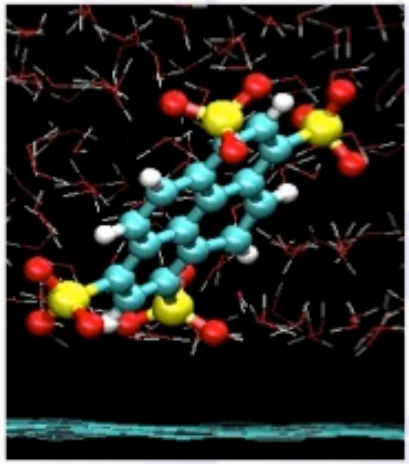
Nanoscale, **5**, 4205 (2013).

UNRAVELING GRAPHENE-MOLECULE-SOLVENT INTERACTIONS









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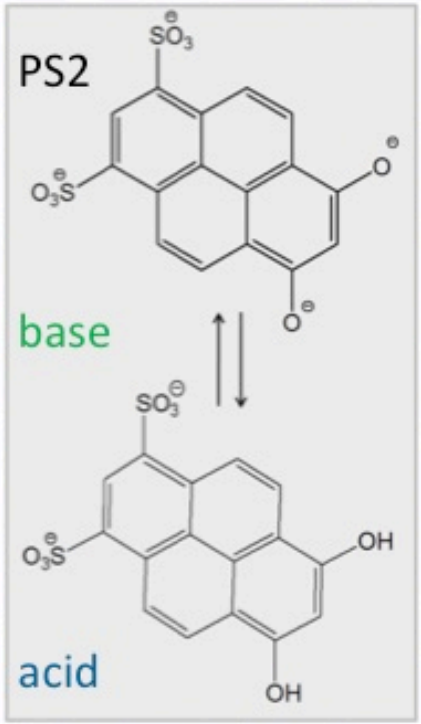
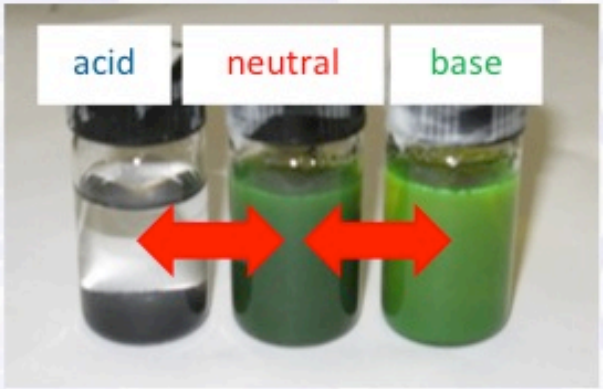
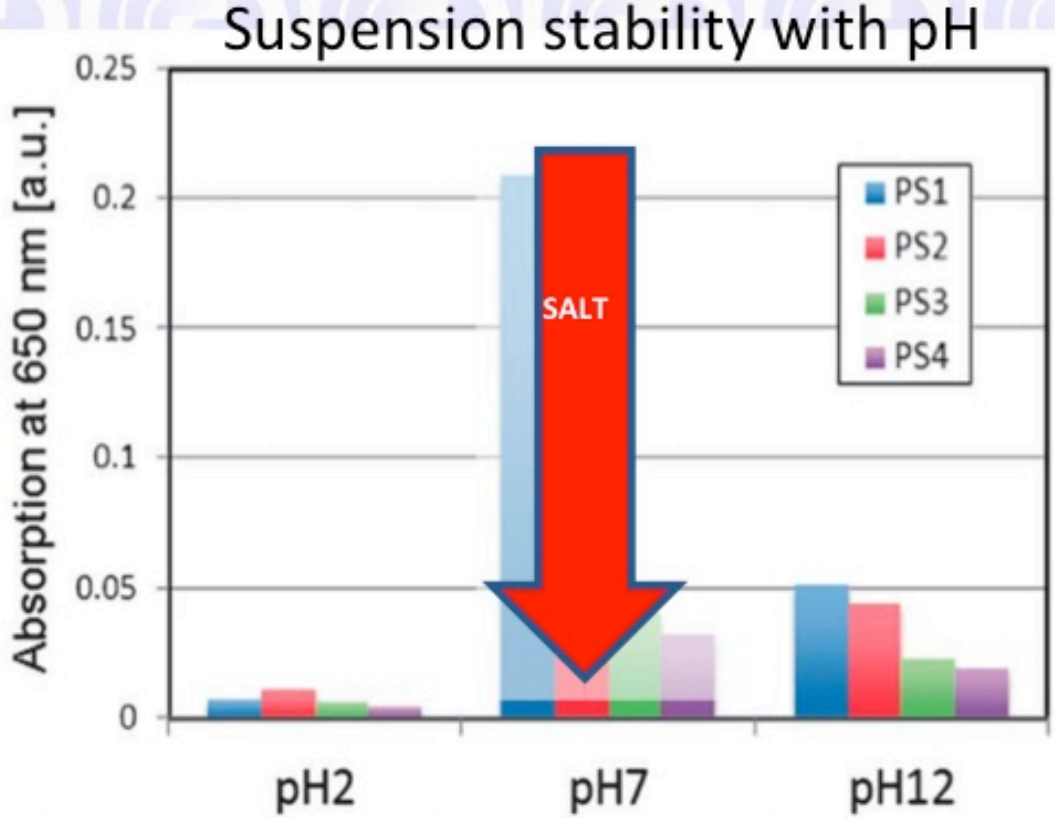
Nanoscale, **5**, 4205 (2013).

UNRAVELING GRAPHENE-MOLECULE-SOLVENT INTERACTIONS







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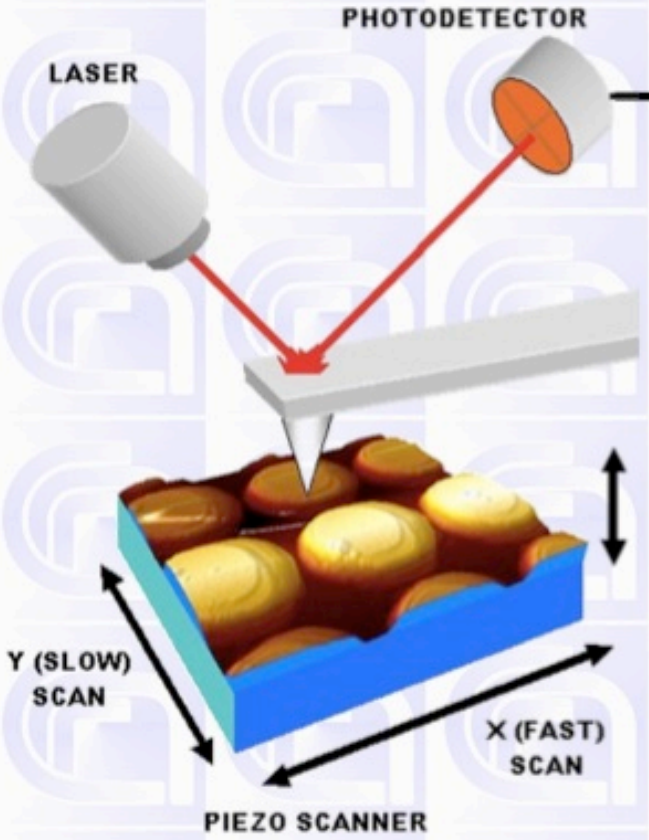
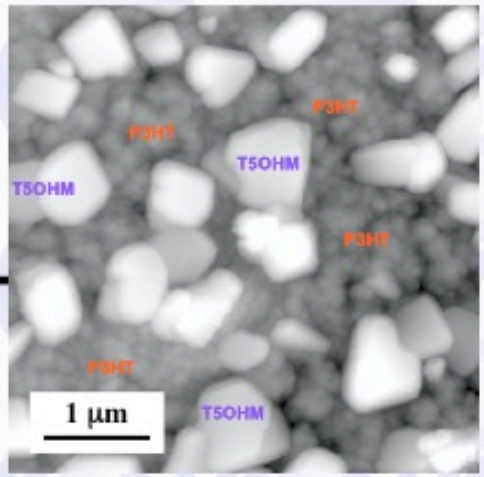
Kelvin Probe Force Microscopy

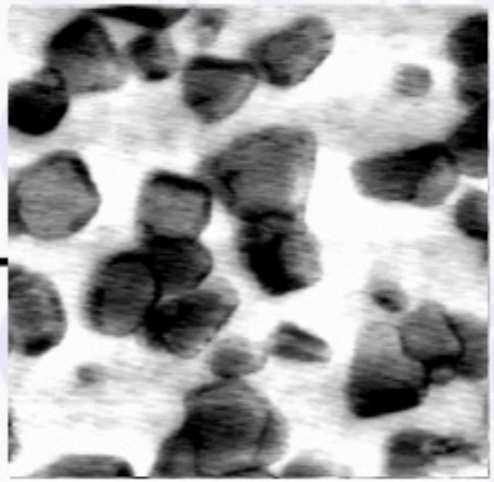


AFM



Topography

KPFM



Potential (Light)

- Maps the electric potential with resolution of few nm and few mV.
- Contactless, minimal perturbation of sample potential.
- Can be performed on working devices (transistors, photovoltaic blends)

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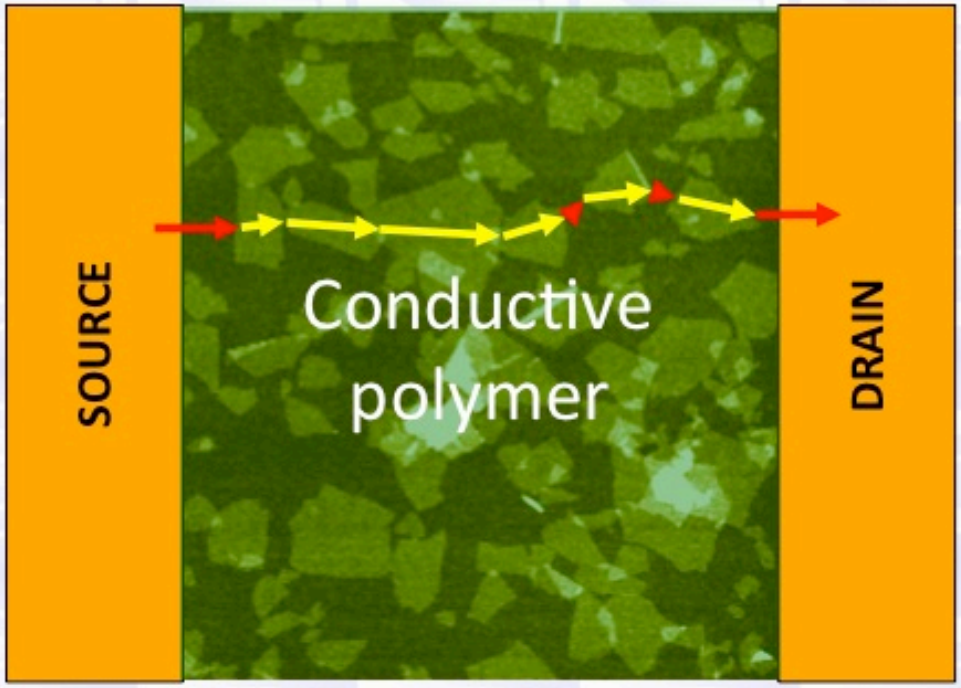
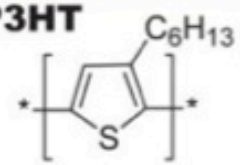
Review paper: Palermo, V., *et al.*, Advanced Materials, (2006) **18**, 145.

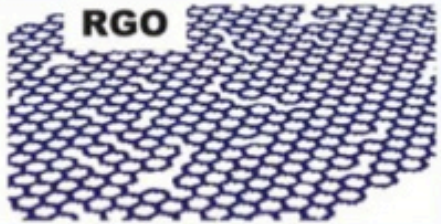
Improved charge mobility in Polythiophene-RGO FET



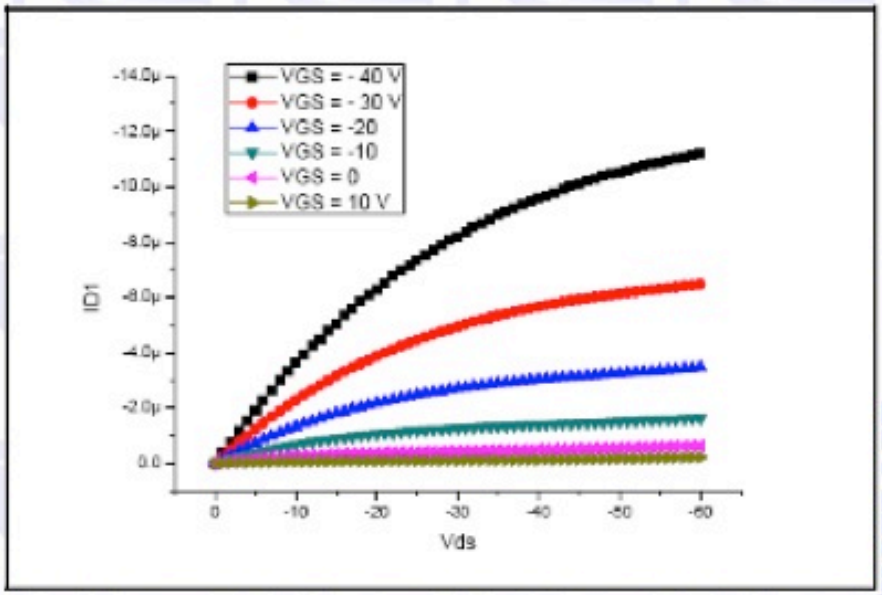
P3HT



RGO



I_{ON}/I_{OFF} ratio = 10^3 - 10^5

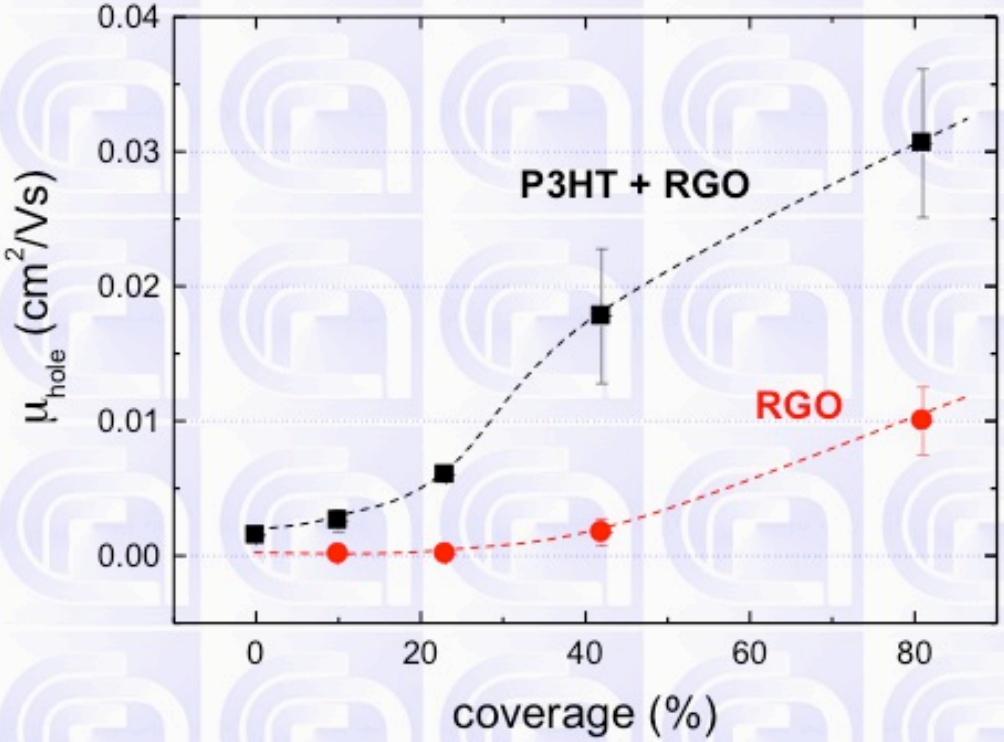


J. Mater. Chem., 2011, **21**, 2924

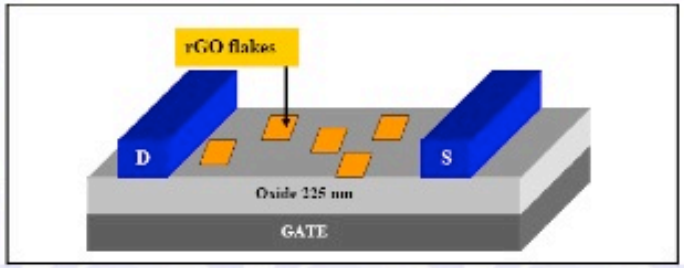
Charge transport in graphene–polythiophene blends as studied by Kelvin Probe Force Microscopy and transistor characterization†

Andrea Liscio,[a] Giulio Paolo Veronese,[b] Emanuele Treossi,[a] Francesco Suriano,[b] Francesco Rossella,[c] Vittorio Bellani,[c] Rita Rizzoli,[*b] Paolo Samorì[*a] and Vincenzo Palermo[*a]

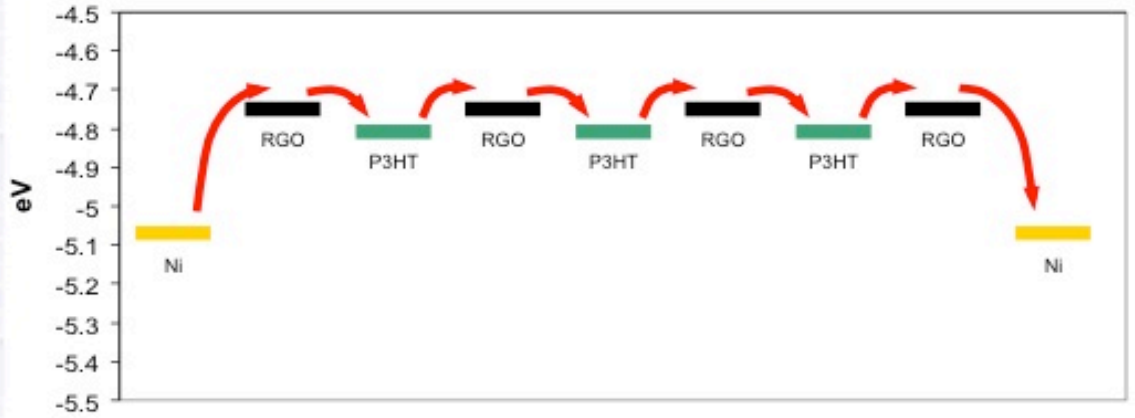
Improved charge mobility in P3HT-RGO FET



FET characterization



I_{ON}/I_{OFF} ratio ~ 10^5



KPFM measurement of work function

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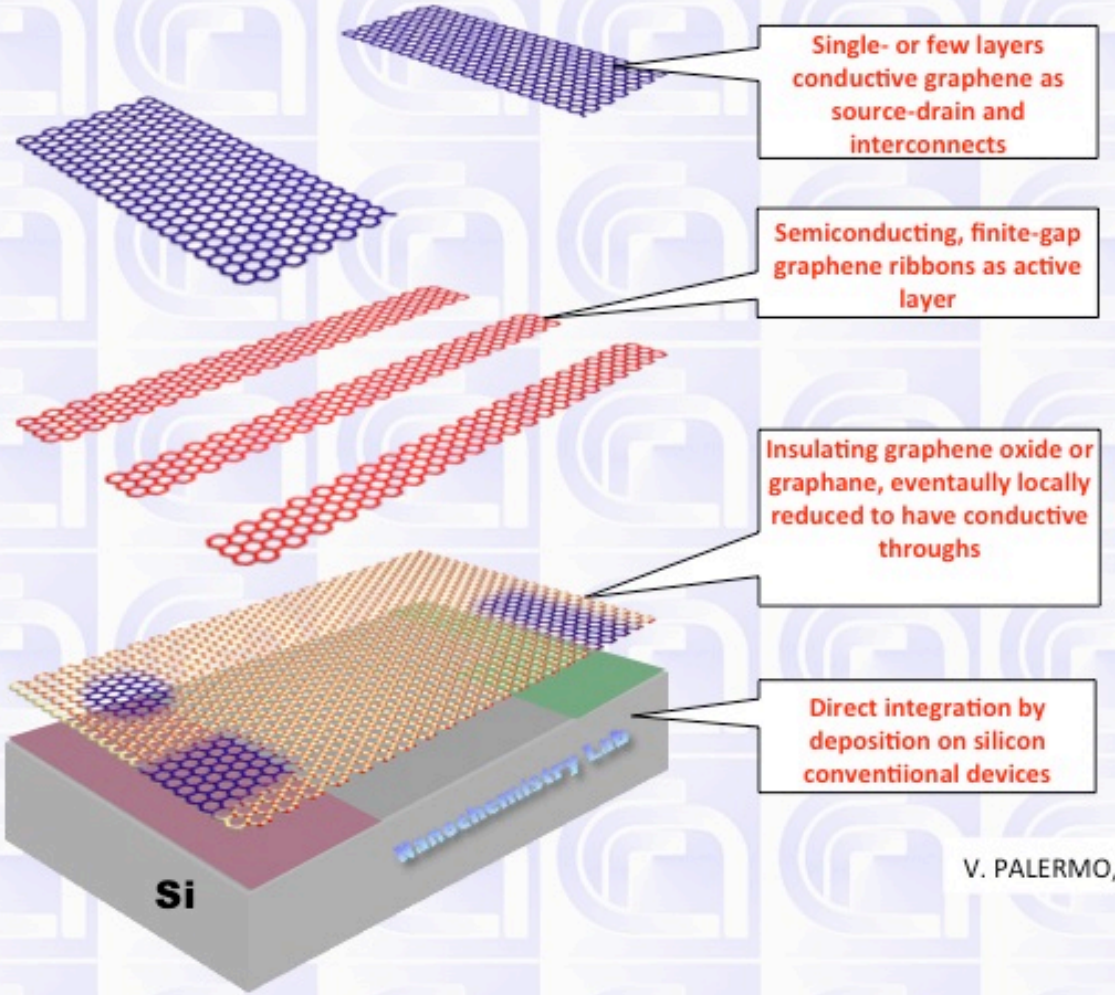
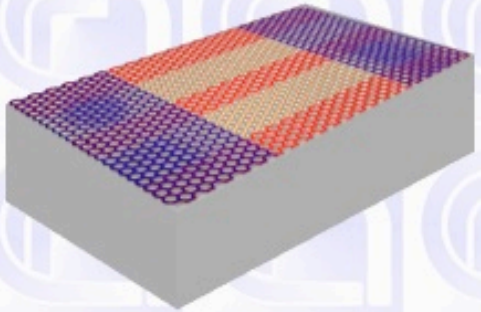
ALL-GRAPHENE ELECTRONICS?



ALL-GRAPHENE FET ?



V. PALERMO, *Chem. Commun.*, 2013, **49**, 2848

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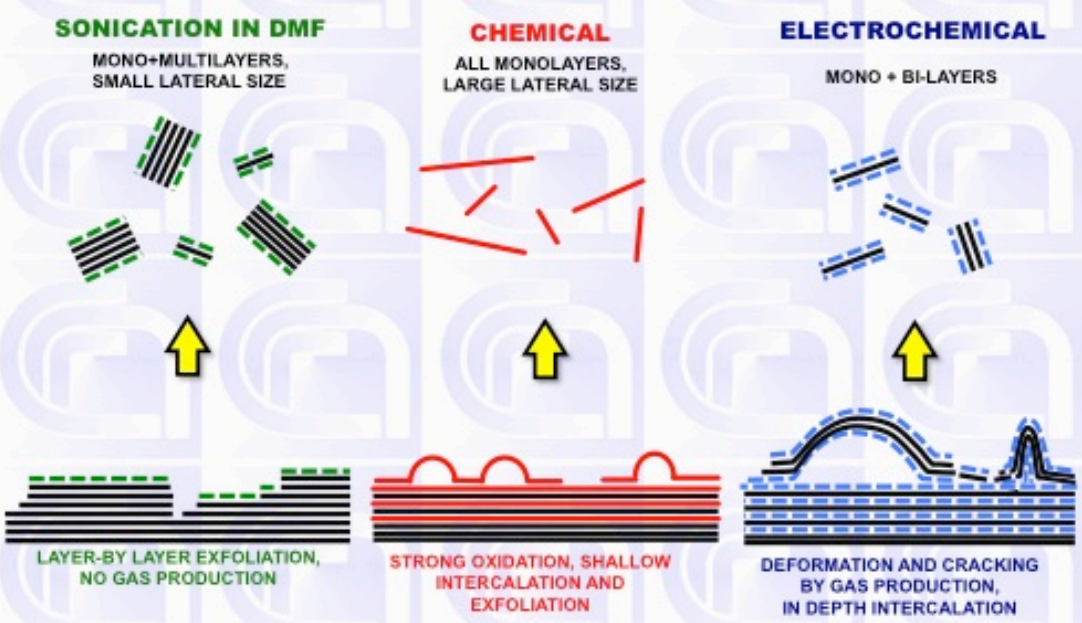
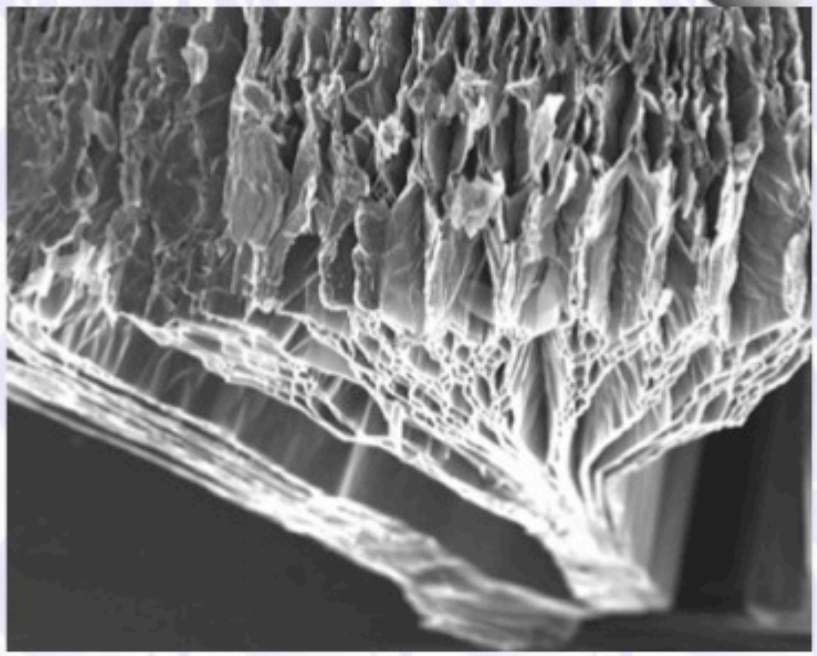
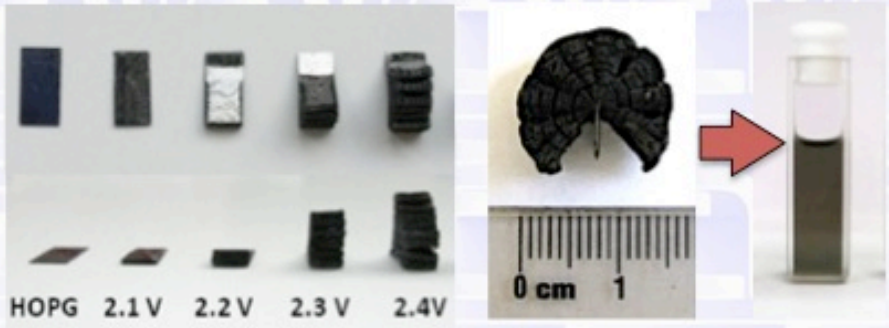
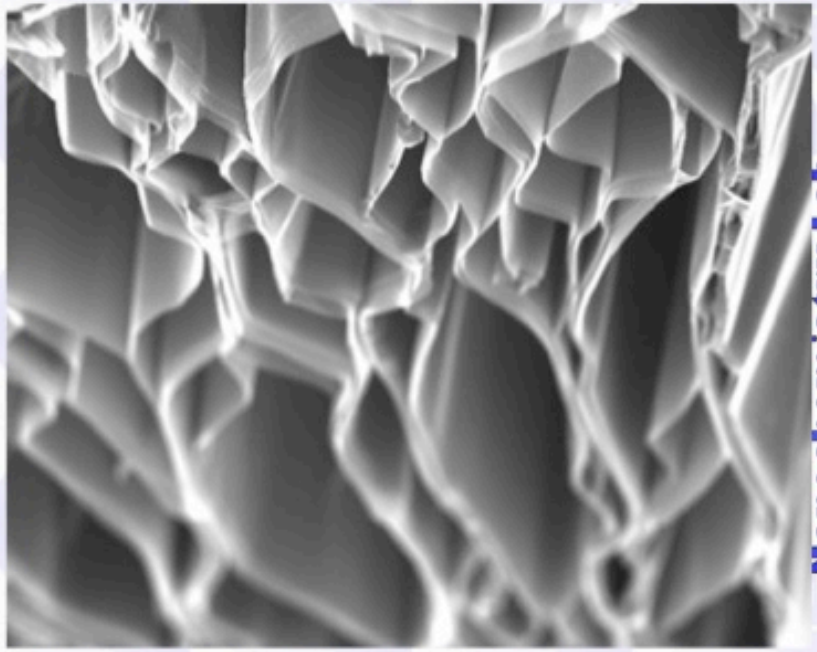
SYSTEMATIC COMPARISON OF GRAPHITE EXFOLIATION PROCESS





ELECTROCHEMICAL EXFOLIATION





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Adv. Func. Mat., in print

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Not a molecule, not a polymer, not a substrate... the many faces of graphene as a chemical platform

Vincenzo Palermo*

GRAPHENE OXIDE PROCESSING AND FUNCTIONALIZATION

Journal of the American Chemical Society, (2011) **133**, 14320.
Journal of the American Chemical Society, (2010) **132**, 14130
Journal of the American Chemical Society, (2009) **131**, 15576.
Journal of Materials Chemistry, (2011) **21**, 2924.
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Langmuir, (2012) **28**, 5489.
Journal of Physical Chemistry C, (2013)**117**, 10683.

SELF ASSEMBLY OF ORGANIC MOLECULES

Advanced Functional Materials, (2007) **17**, 3791.

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Nanoscale, **5**, 4205 (2013).
Carbon, **53**, 357 (2013).
Advanced Functional Materials, DOI: 10.1002/adfm.201203686 (2013).
Organic Electronics, **14**, 1787 (2013).

SELF-ASSEMBLY ON MULTIPLE SCALES

Angewandte Chemie-International Edition, (2007) **46**, 4428.

SMALL MOLECULES AND POLYMERS

Advanced Materials, (2010) **22**, E81.
Journal of the American Chemical Society, (2009) **131**, 7055.
Advanced Functional Materials, (2008) **18**, 3947.
Journal of the American Chemical Society, (2008) **130**, 14605.