Materials Science and Nanotechnology Laboratory

Molecularly Imprinted Mesoporous Materials via Sol-Gel Processing:

Graphene Enhanced Raman Scattering meets molecular imprinting

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X Workshop Italiano Sol-Gel

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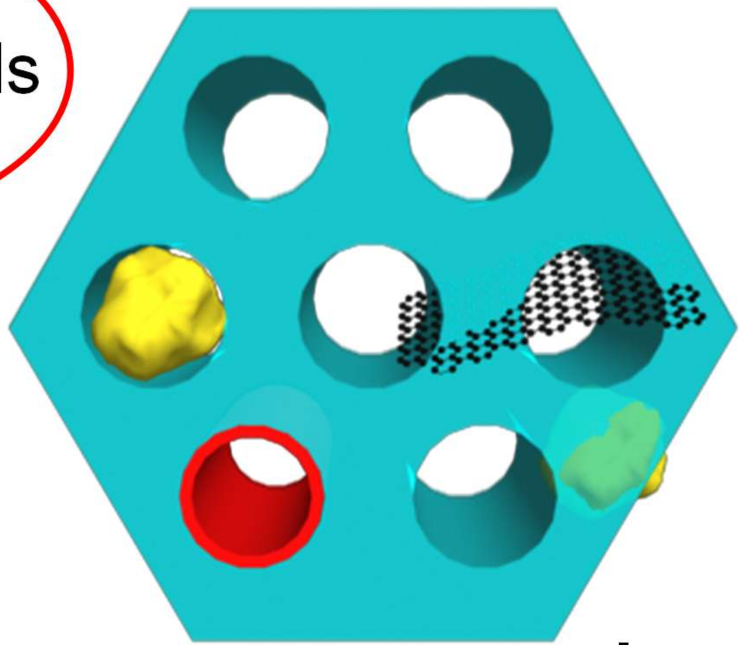
Multifunctional nanoporous materials

Inclusions
in the pore walls
in the pores

P. Innocenzi, L. Malfatti, D. Carboni. **Nanoscale** 2015, 7, 12759-12772.



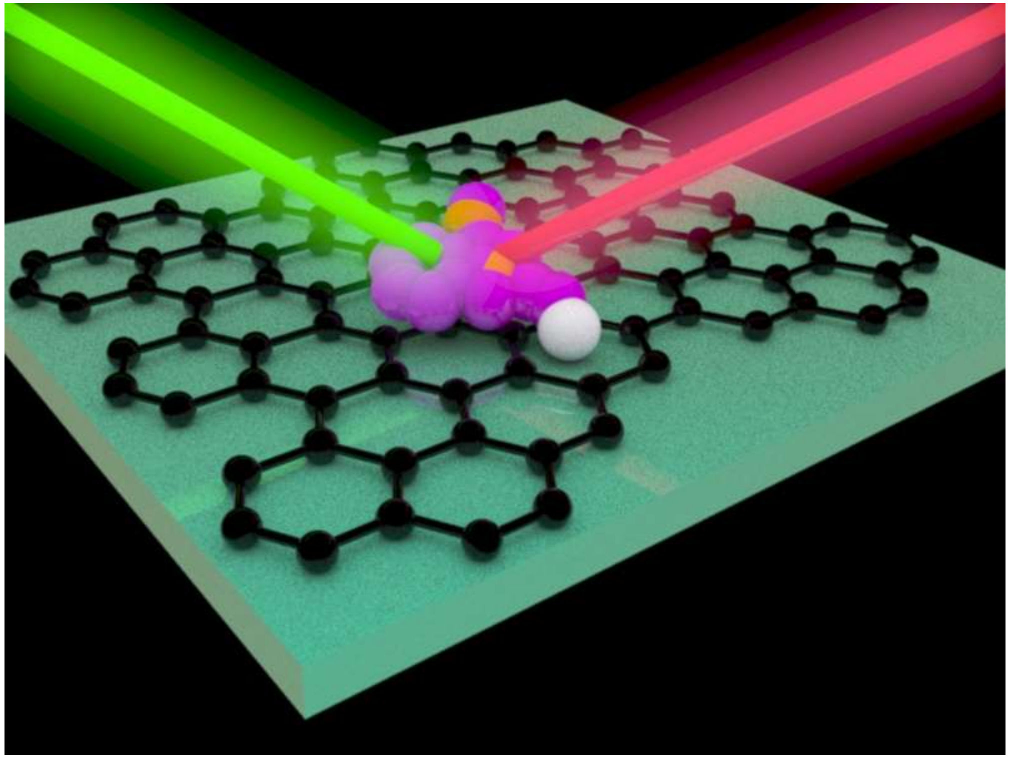
Pore symmetry
Size
Shape
accessibility

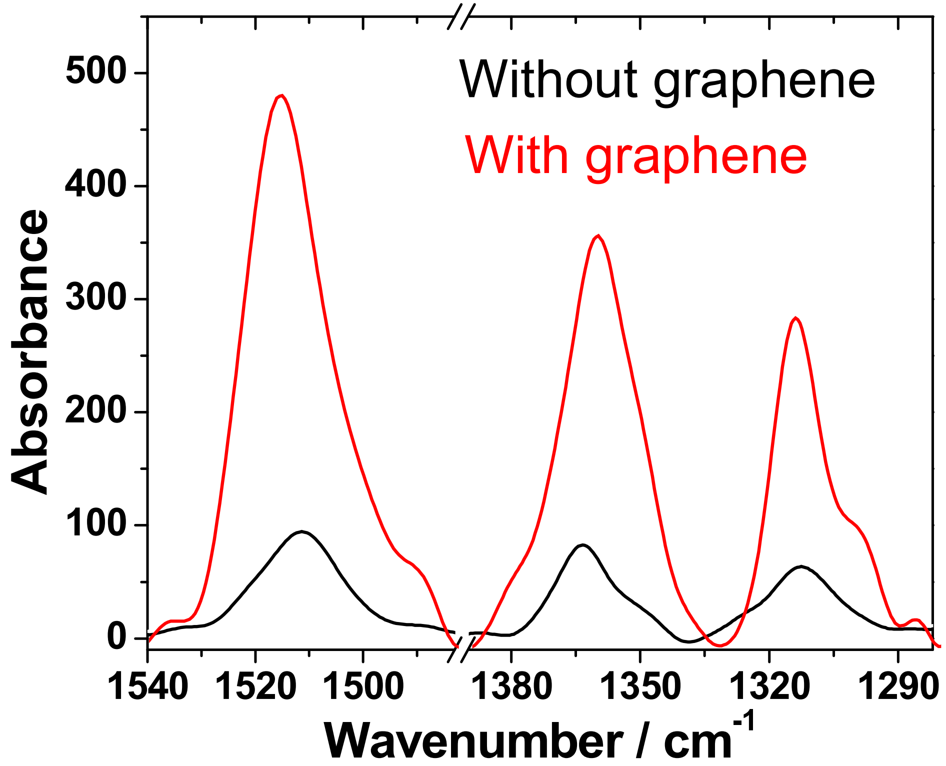
Pore surface
acidity
chemical modification

Inorganic framework
crystallinity
Bulk properties (n, E)
wall thickness
wall nature (composition, porosity)

G. J. de A. A. Soler-Illia, E. Crepaldi, D. Grosso and C. Sanchez. **Current Opinion Colloid Interf. Sci.**, 2003, 8, 109-126.

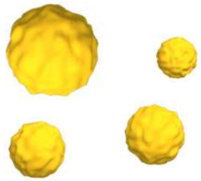
Graphene enhanced Raman scattering (GERS)



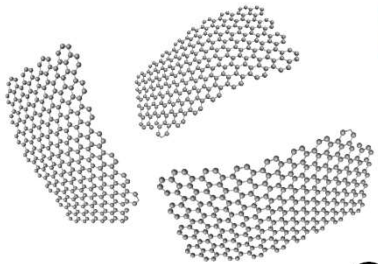


GERS effect can be used to amplify the intensity of the Raman spectrum provided by a specific molecule

X. Ling et al. Nano Lett. **2010**, 10, 553−561.

SERS 

Electromagnetic enhancement

 GERS

Chemical enhancement

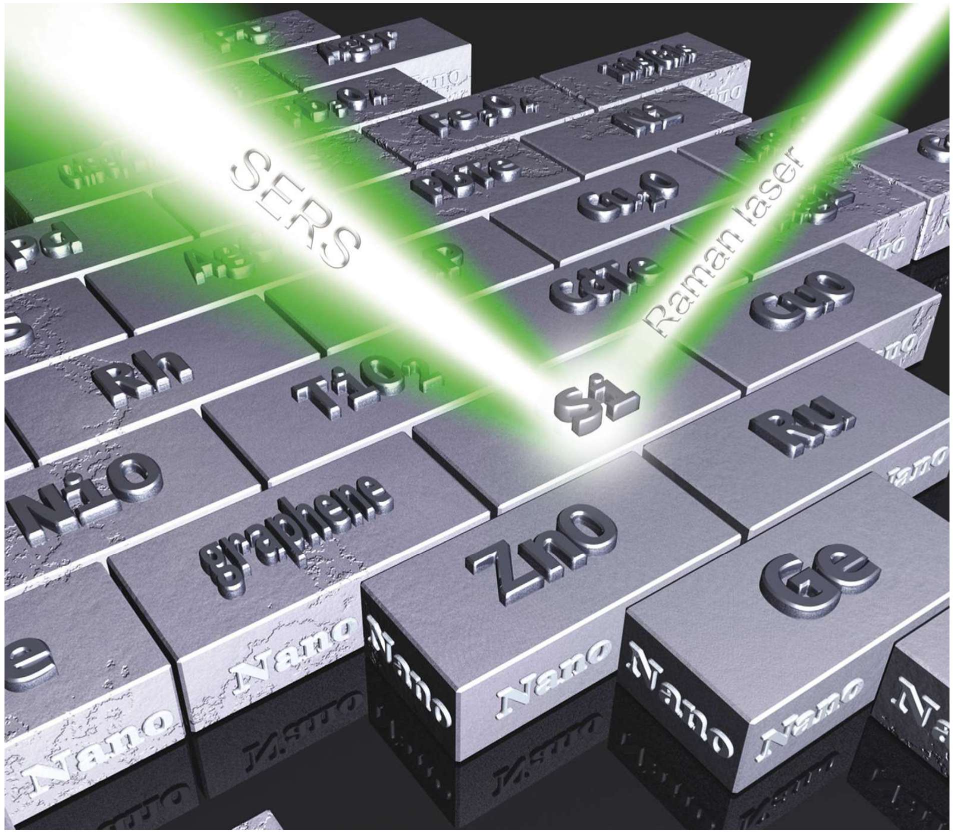
SERS		GERS
↑	Enhancement Factor	↓
↓	Laser Stability	↑
↑	Cost	↓
↓	Selectivity	↓

Towards a low-cost improvement of GERS

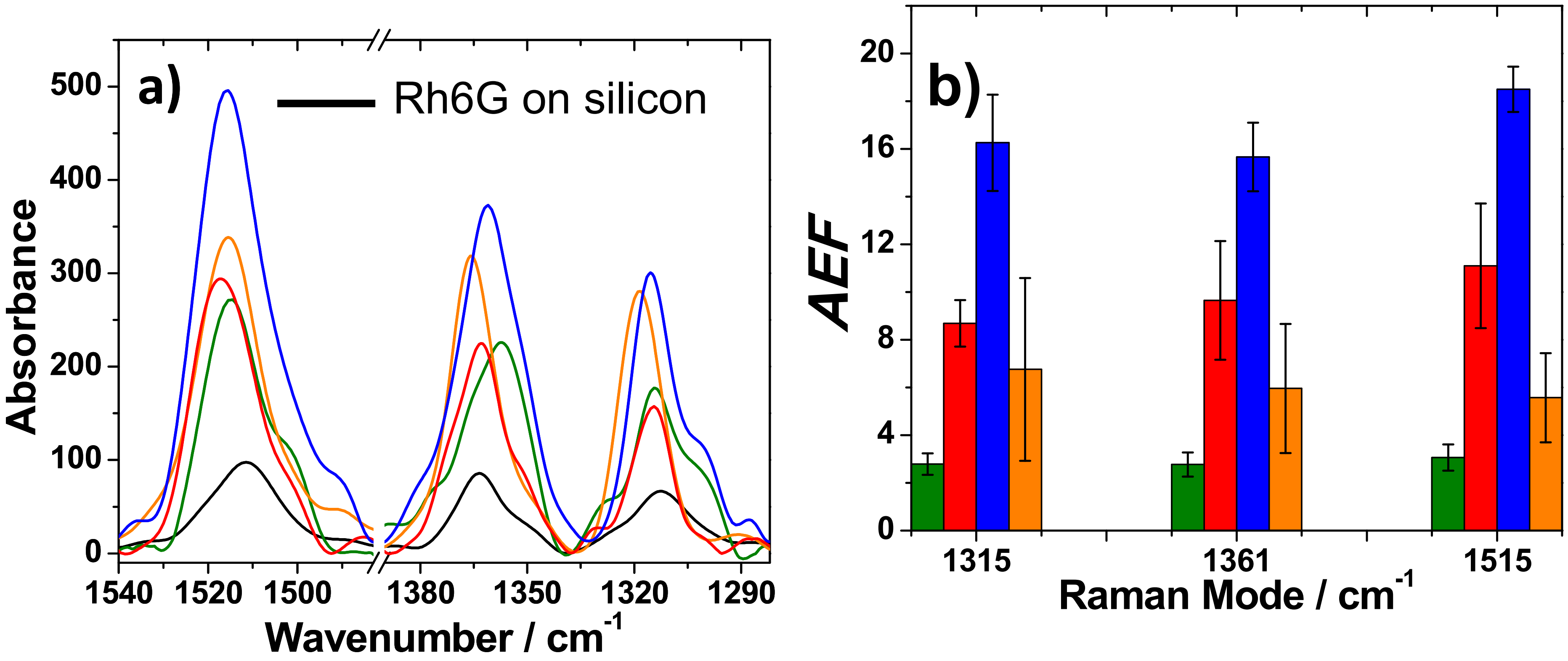
Enhanced Raman Scattering from non-Group 11 (Ag, Cu, Au) nanostructures such as transition metals oxides and semiconductors

X. Wang, W. Shi, G. Shea, L. Mua
Phys. Chem. Chem. Phys., 2012, **14**, 5891–5901

The enhancement is associated with the Charge-Transfer (CT) mechanism between the adsorbed analytes and the substrate.



Analytical enhancement factor (AEF)



MP Silica

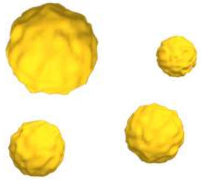
MP Silica + exfoliated graphene

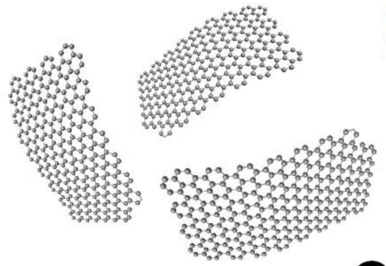
MP Titania (350°C) + exfoliated graphene

MP Titania (450°C) + exfoliated graphene

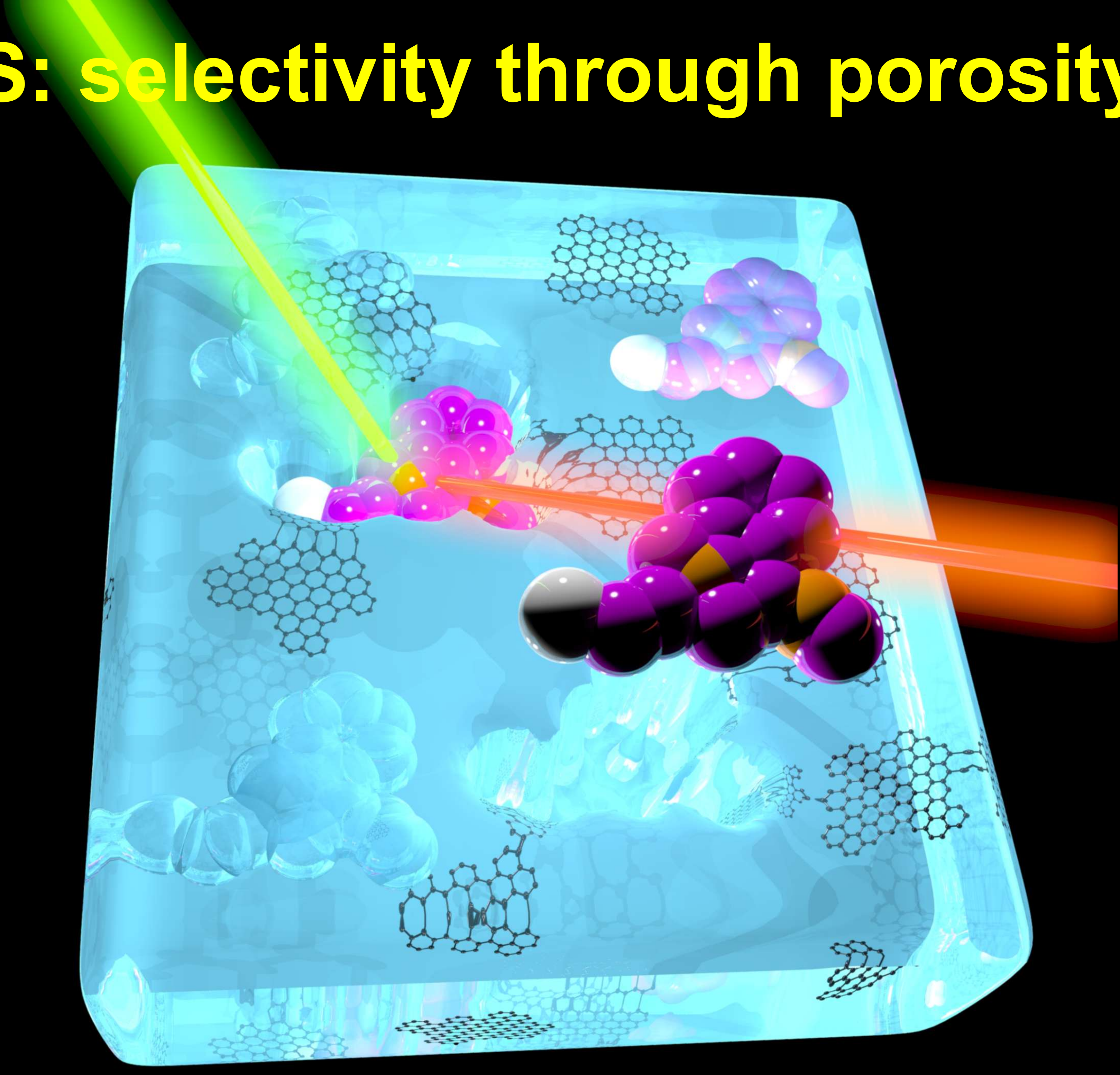
D. Carboni, L. Malfatti et al. *J. Phys. Chem. Lett*, **2015**, *6*, 3149–3154.

SERS		GERS
Electromagnetic enhancement		Chemical enhancement
↑	Enhancement Factor	↓
↓	Laser Stability	↑
↑	Cost	↓
↓	Selectivity	↓

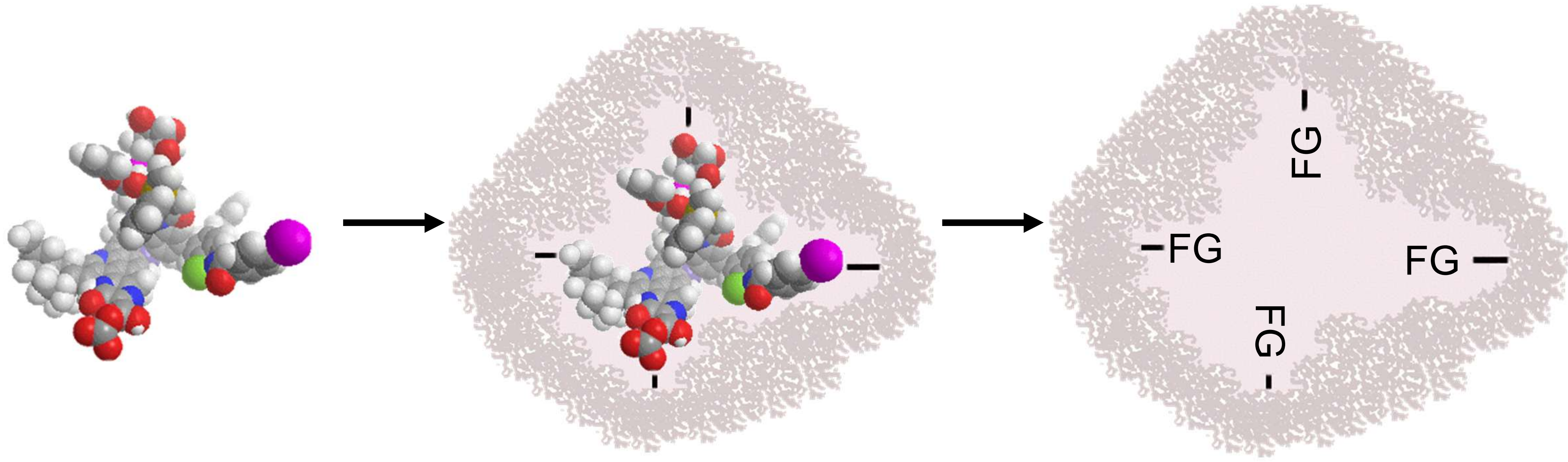




MI-GERS: selectivity through porosity

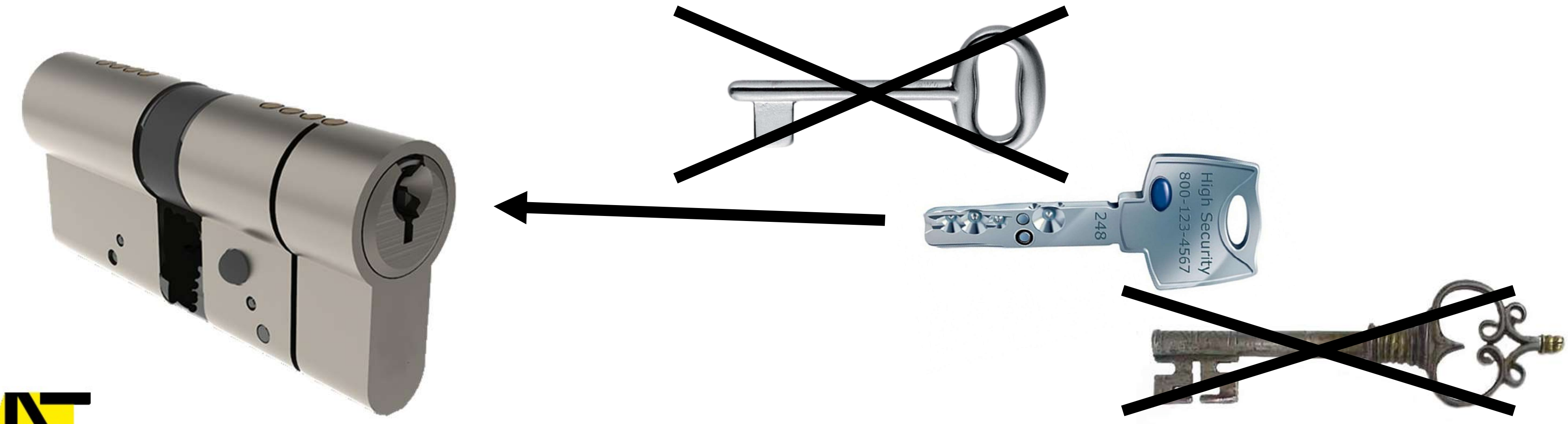


What is molecular imprinting?



1) Imprinting complex　　2) polycondensation　　2) Imprinted cavity

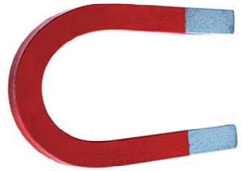
Tailor-made recognition sites for specific molecules!!!



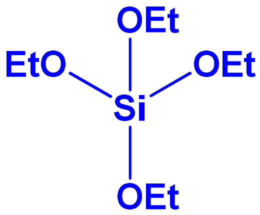
The material's design

+

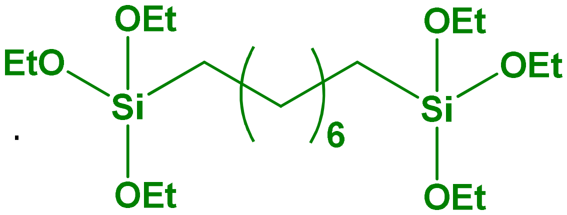
+



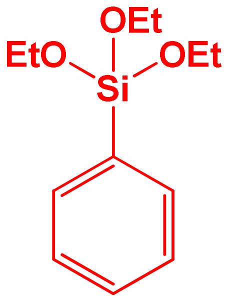
+



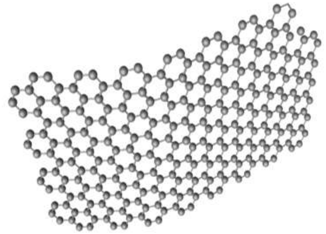
TEOS



B-TES-8



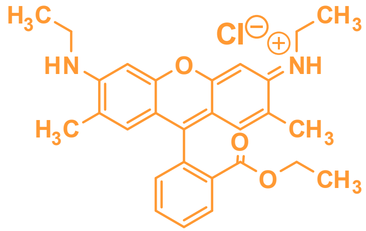
Ph-TES



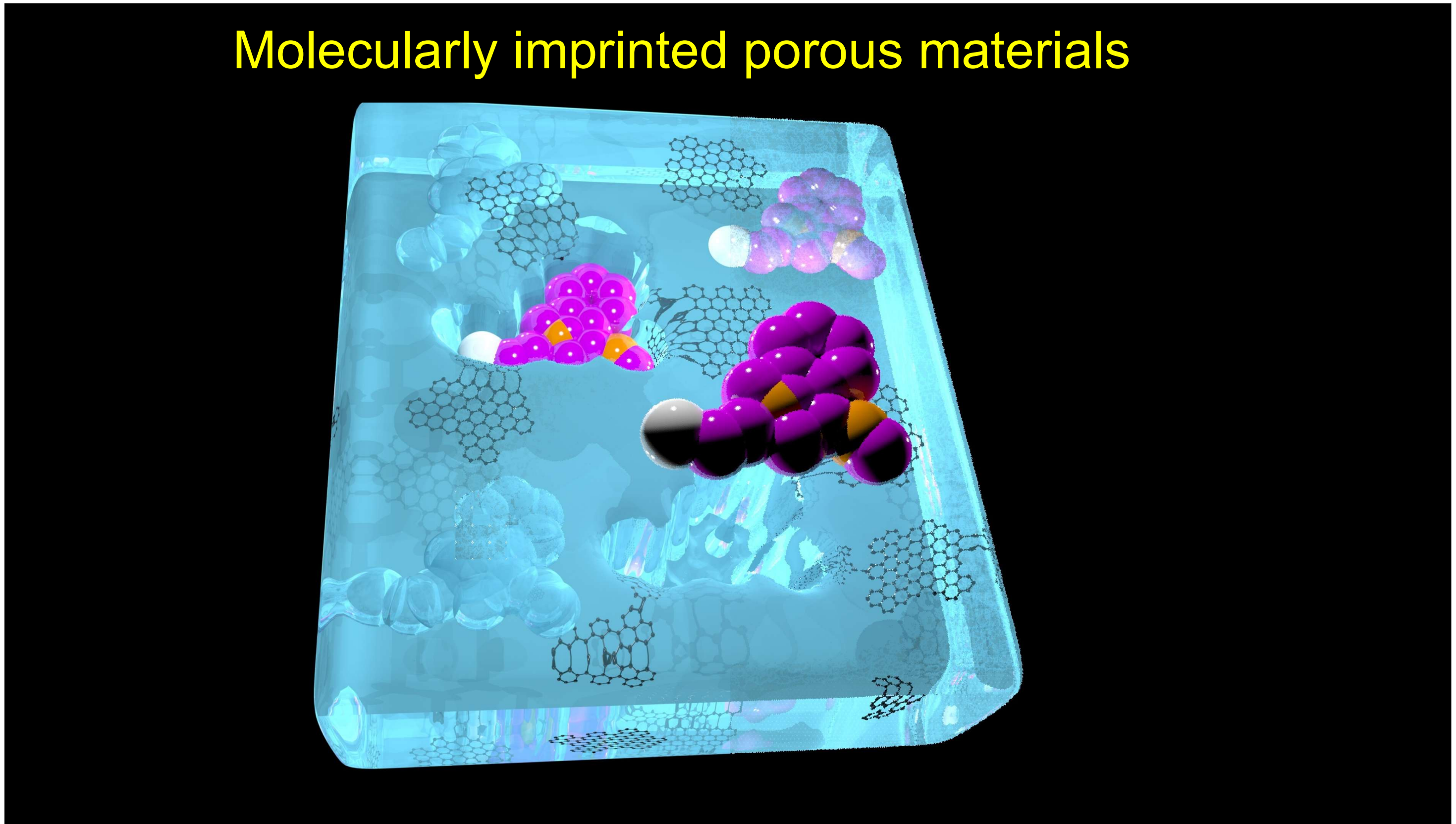
Exfoliated graphene

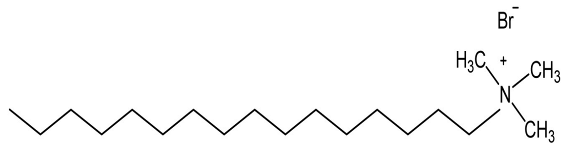
(in NVP)

+



Rhodamine 6G

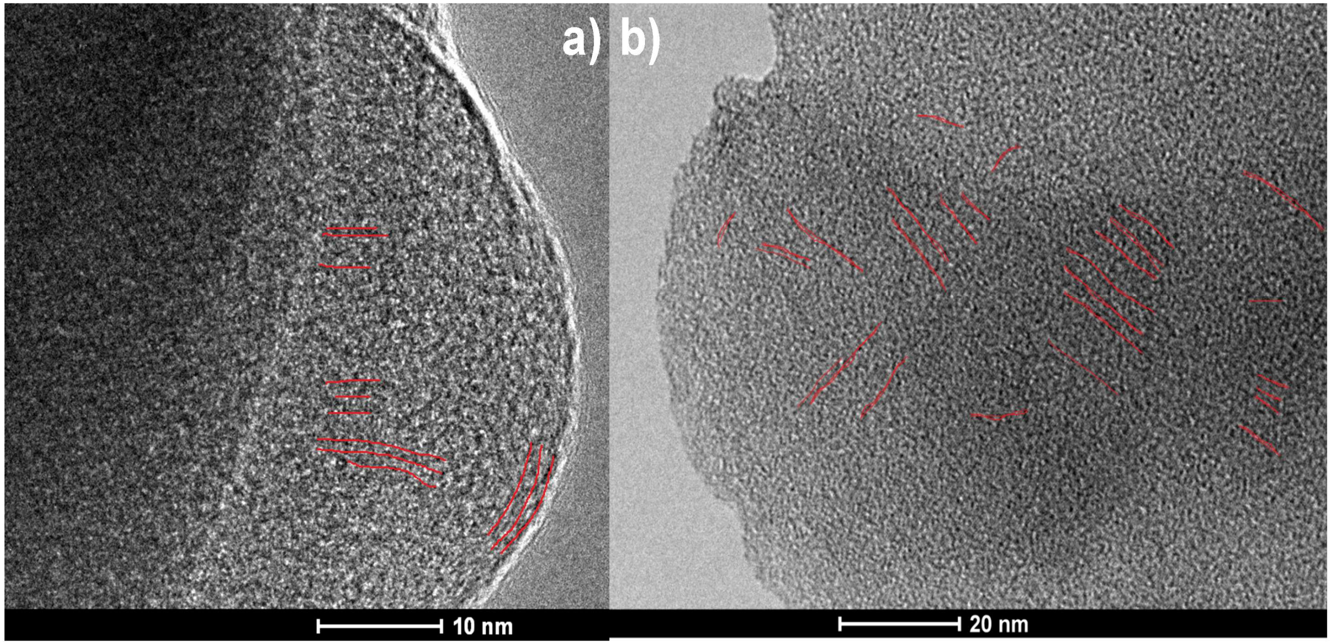




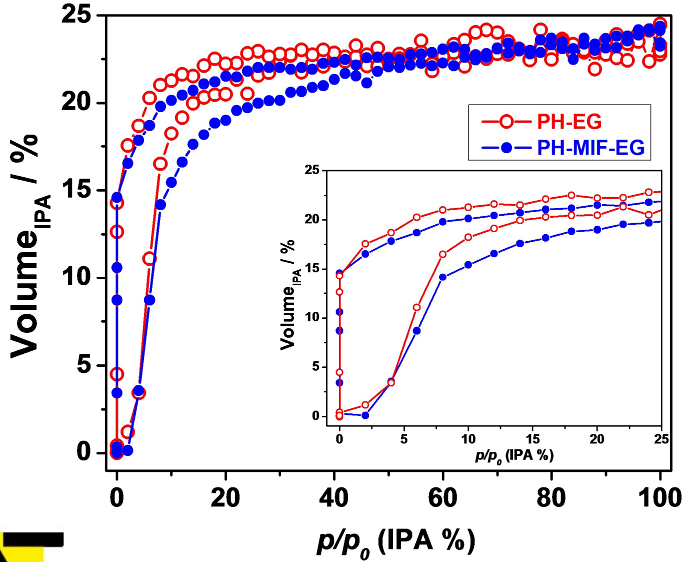
C-TAB

Pore structure

microporous | microporous /molecularly imprinted



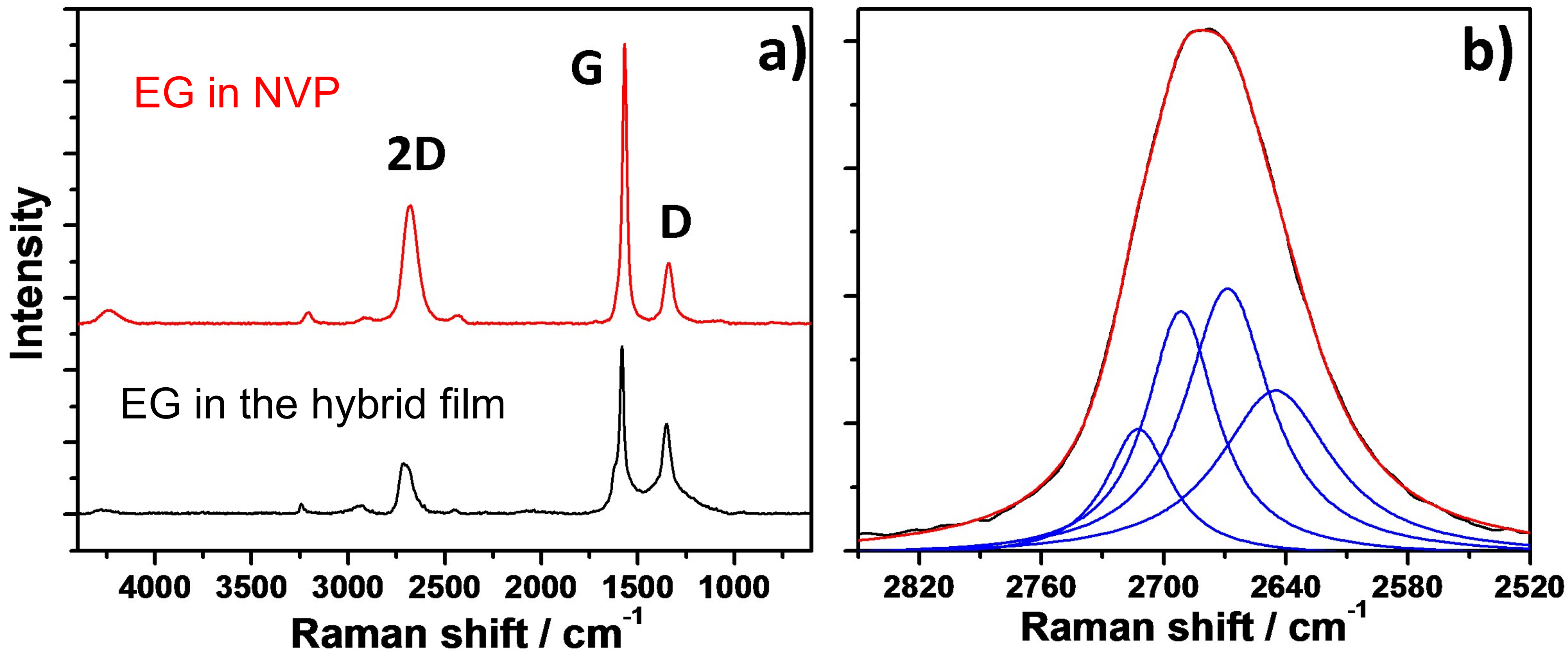
Average **pore size** **1-2 nm** and worm-like type porosity, mostly not organized.



Environmental ellipso-porosimetry on sample treated at 450°C.

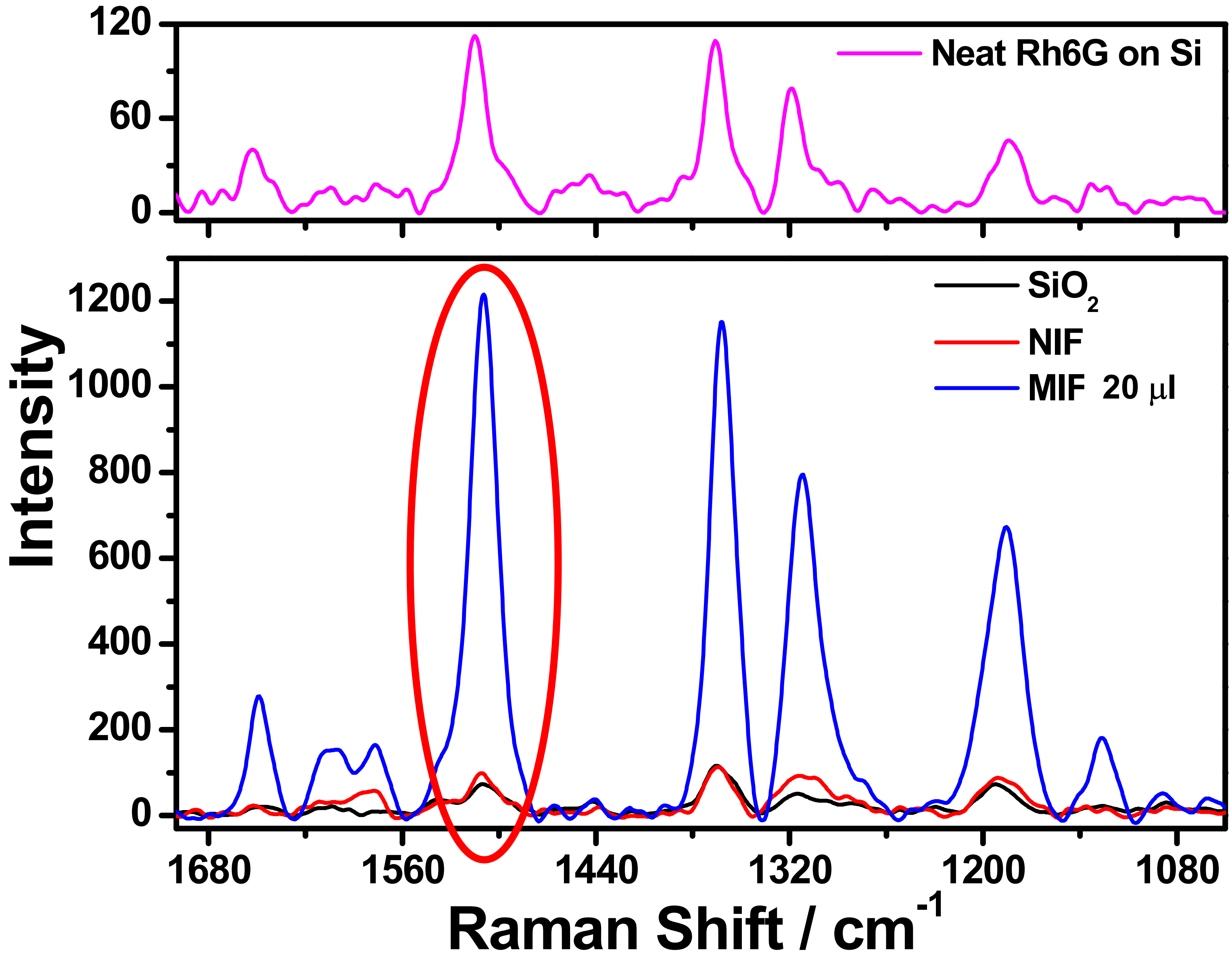
Film thickness ≈ 800 nm

Exfoliated graphene in the hybrid films: Raman characterization



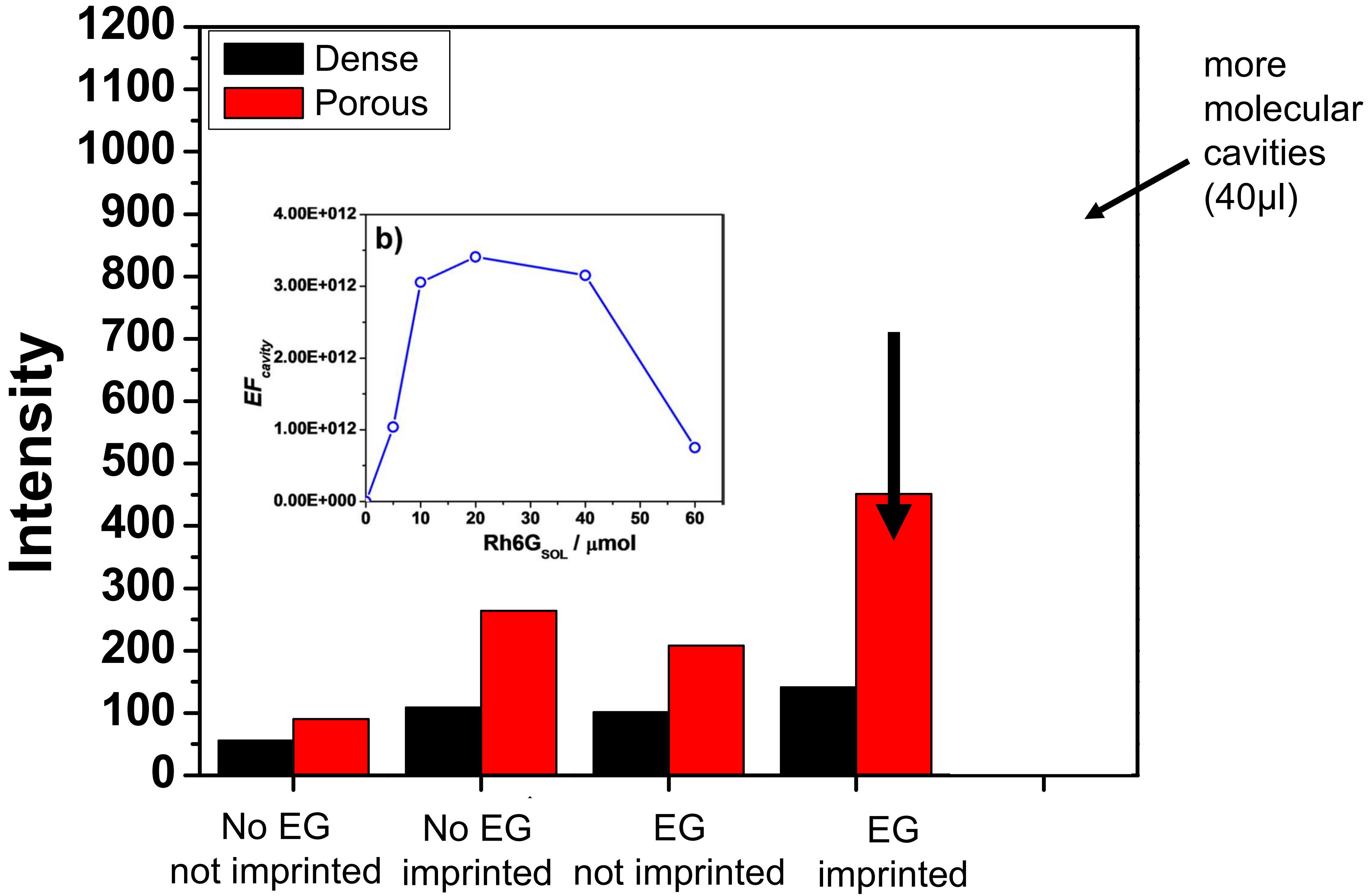
The best fit of the 2D band is obtained using **4 Laurentian curves**, indicating the presence of **graphene bilayers** in the nanocomposites.

Not Imprinted (NIF) *vs* Molecularly Imprinted (MIF)



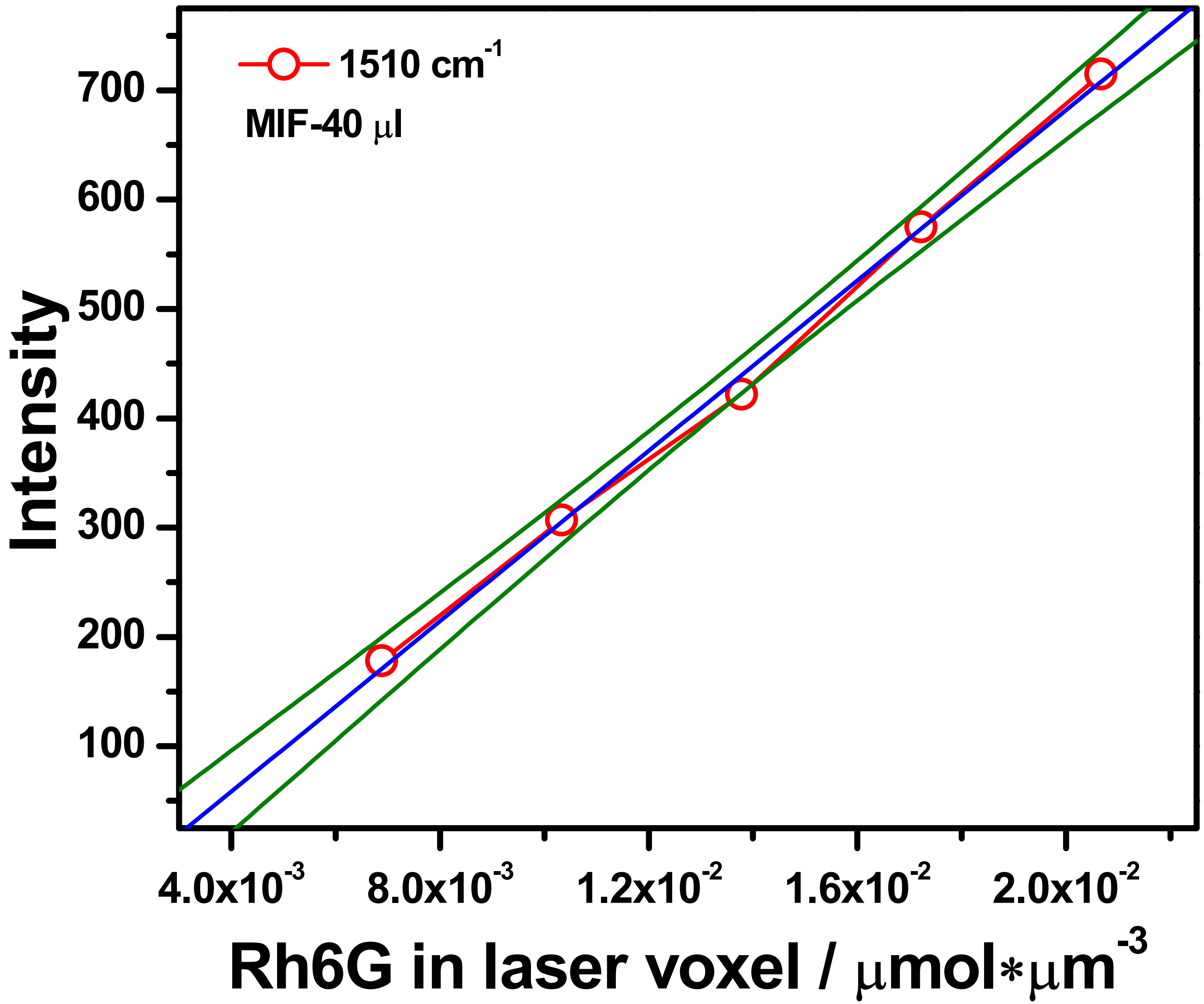
D. Carboni et al., *ACS Appl Mater interfaces*, **2016**, ***8***, 34098-34107.

Molecularly Imprinted (20 µl) GERS



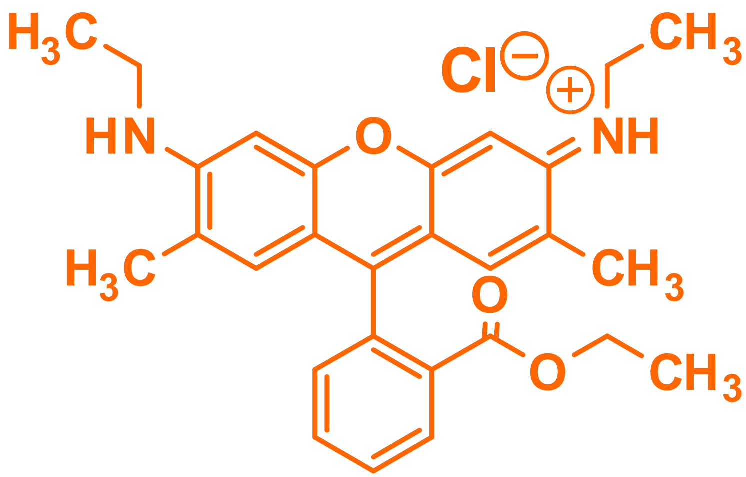
Intensity of the Rh6G Raman band at 1510 cm^{-1}

Linear response & reproducibility

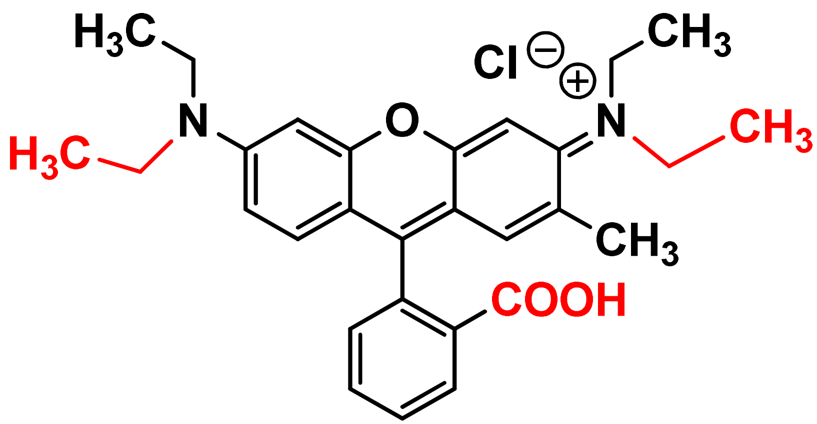


D. Carboni et al., *ACS Appl Mater interfaces*, **2016**, ***8***, 34098-34107.

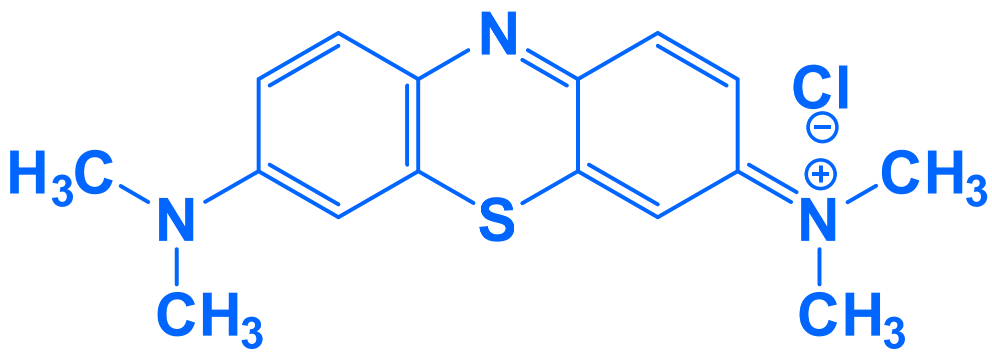
Selectivity in GERS



Rh6G

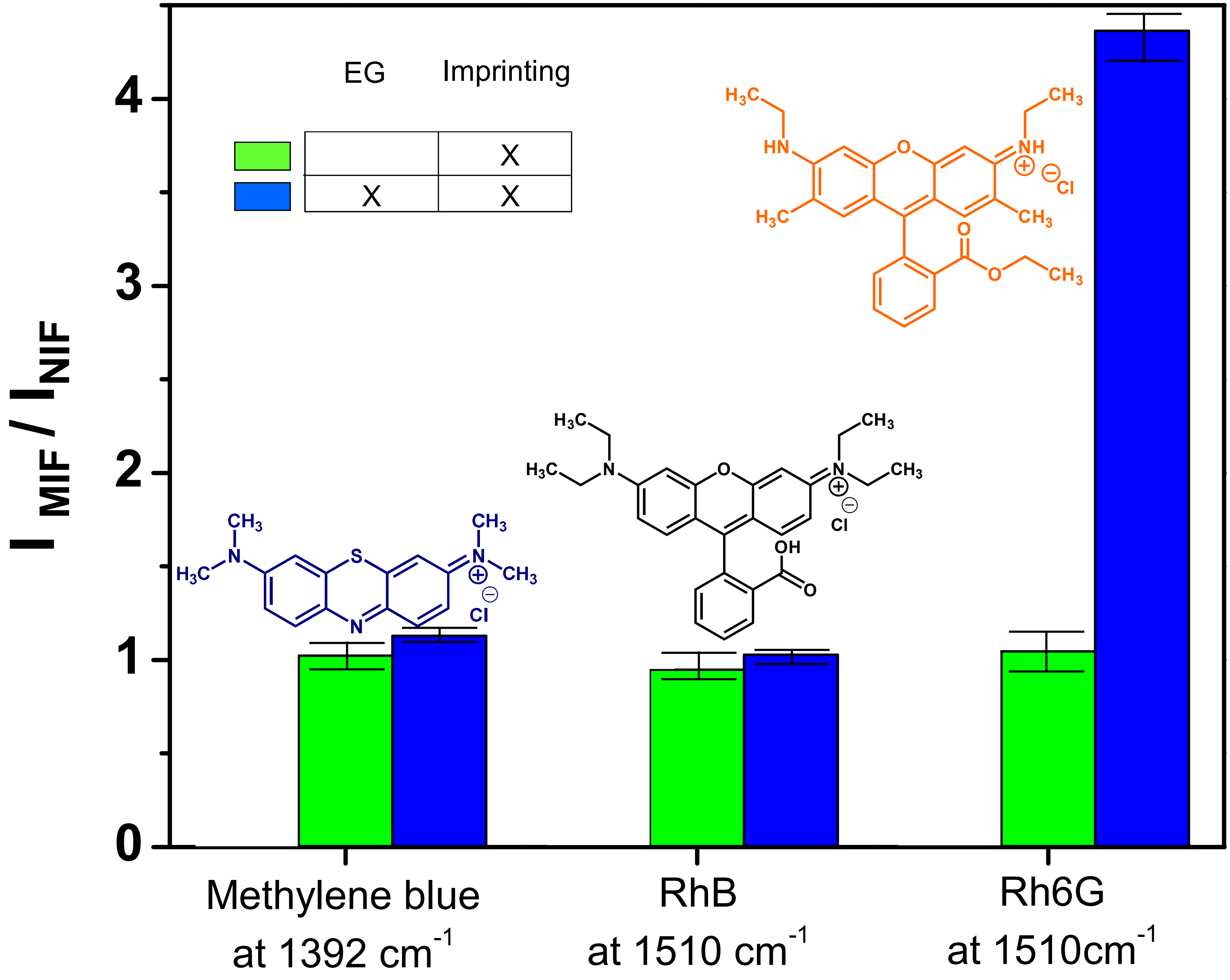


RhB



Methylene Blue

GERS selectivity *vs* Methylene blue, RhB, and Rh6G



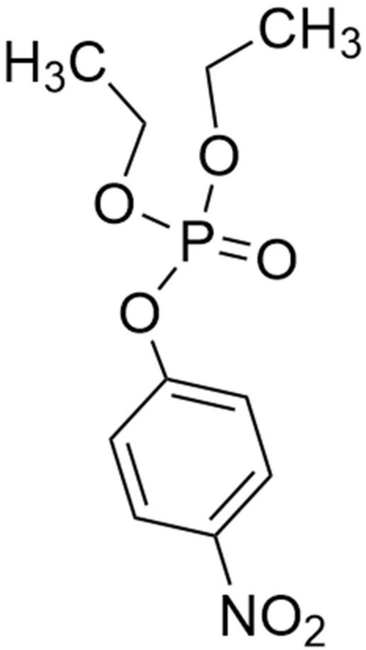
D. Carboni et al., *ACS Appl Mater interfaces*, 2016, 8, 34098-34107.

Detection of pesticides in water

- Organophosphates, such as the **Paraoxon,** are widely used in agriculture as **pesticides**.

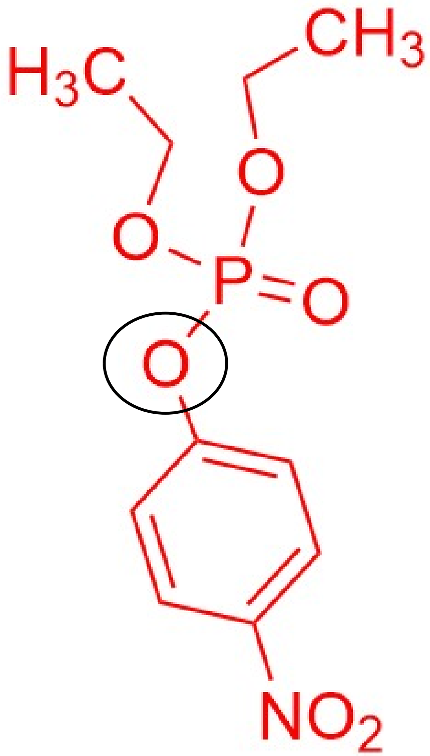
- These compounds are the most widespread classes of **pollutants** among the highly toxic organic pollutants (HTOPs)

- The persistency in the environment is a high threat for the human health since they can produce **neurotoxic effects** and also death.



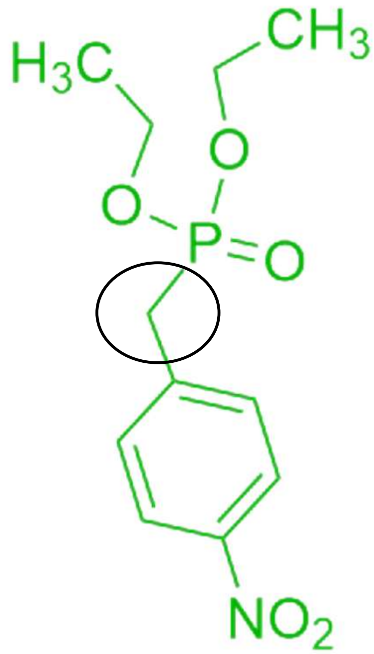
paraoxon

Template selection for molecular imprinting



Paraoxon = **diethyl 4-nitrophenyl phosphate**

- Highly toxic
- Can be slowly hydrolyzed in protic solvent

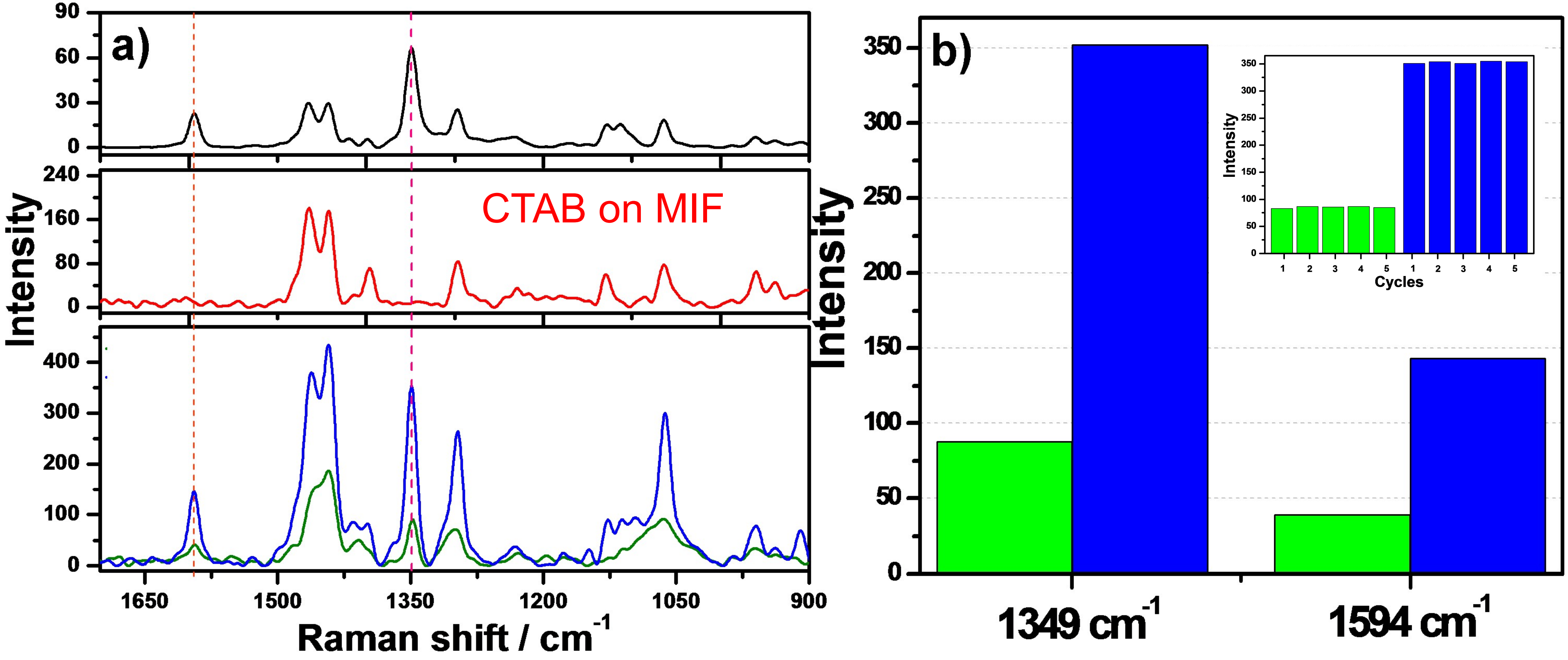


4NBP = **diethyl(4-nitrobenzyl)phosphonate**

- Structural analogue of the Paraoxon
- Less toxic
- It can not be hydrolyzed

Raman modes for MIGERS sensing

Paraoxon + CTAB on SiO_2



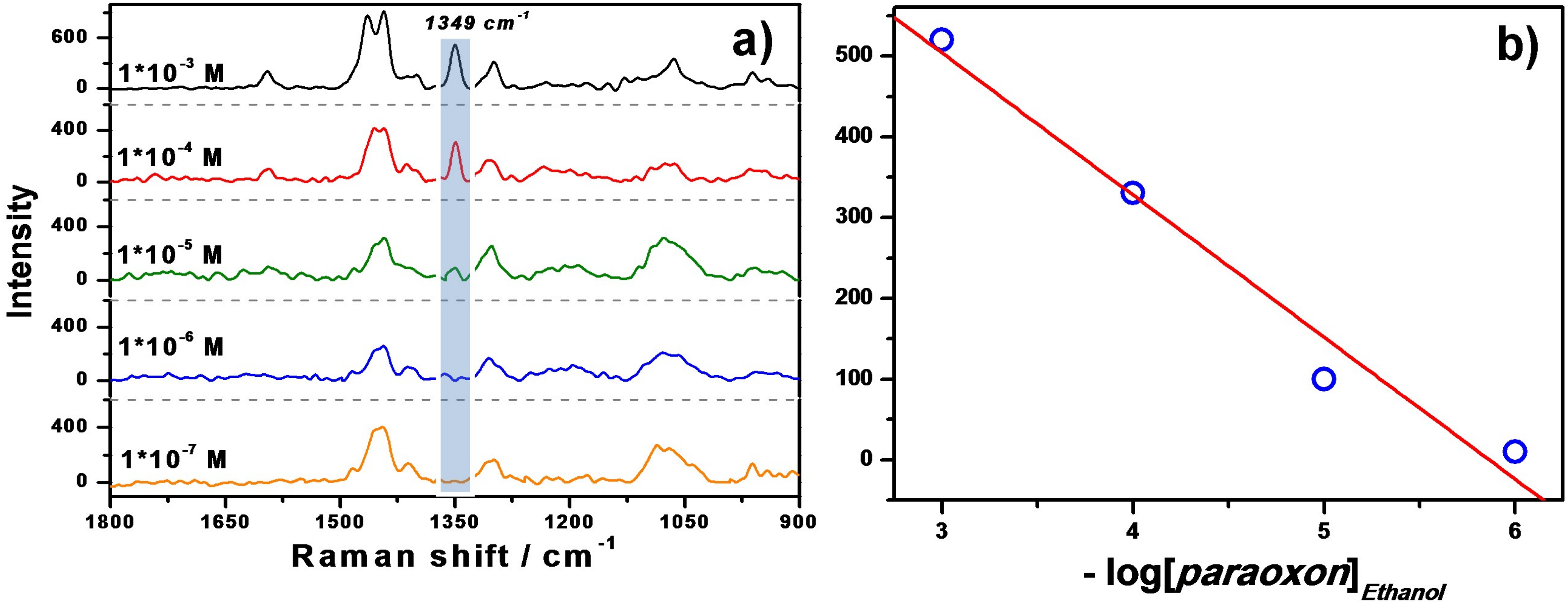
Paraoxon + CTAB on MIF

Paraoxon + CTAB on NIF

MIF *vs* NIF
4X signal amplification

D. Carboni et al., *J. Raman Spectr.*, **2018,** 49, 189-197

Raman Intensity *vs* concentration in Ethanol



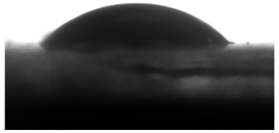
GERS spectra of paraoxon in ethanol (v/v=1:10) solution measured on imprinted substrates.

D. Carboni et al., *J. Raman Spectr.*, **2018,** 49, 189-197

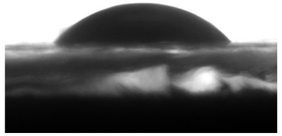
Raman Intensity *vs* concentration in H_2O/Ethanol

NIF	**44.28°**
MIF	**44.08°**

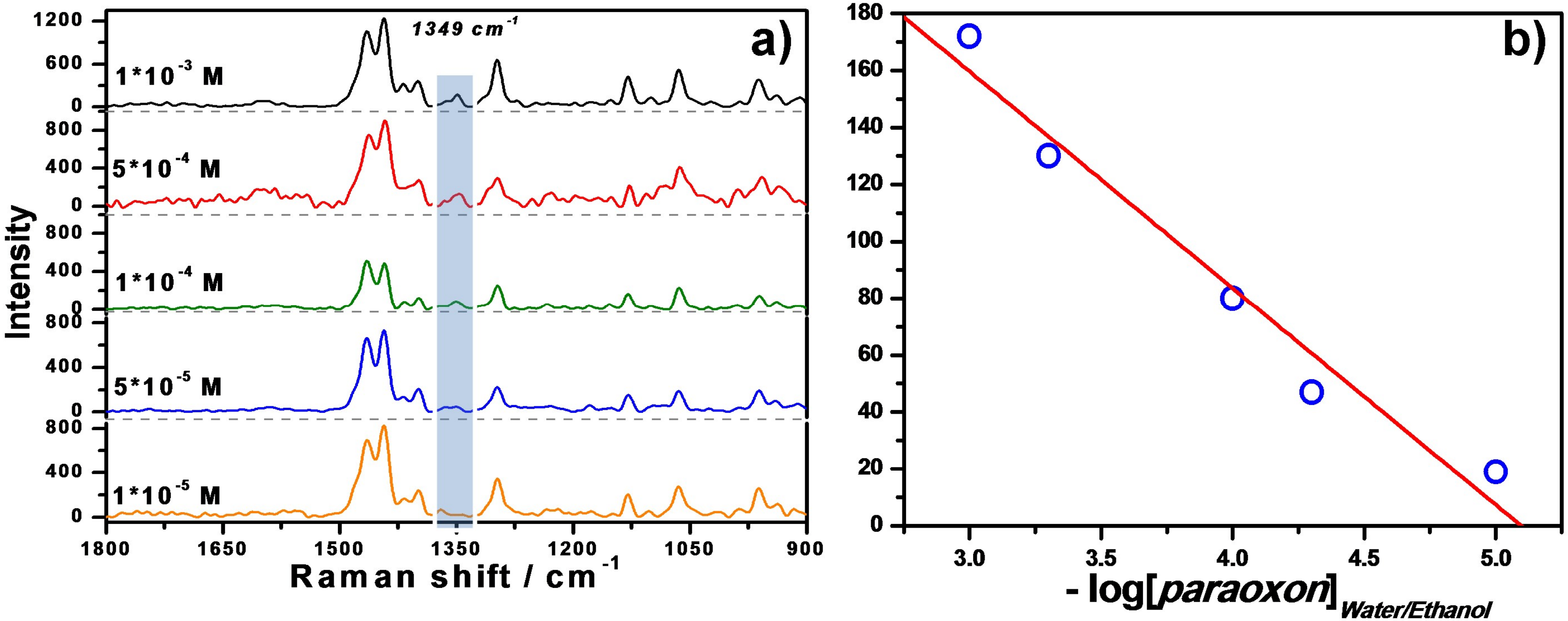
NIF



MIF



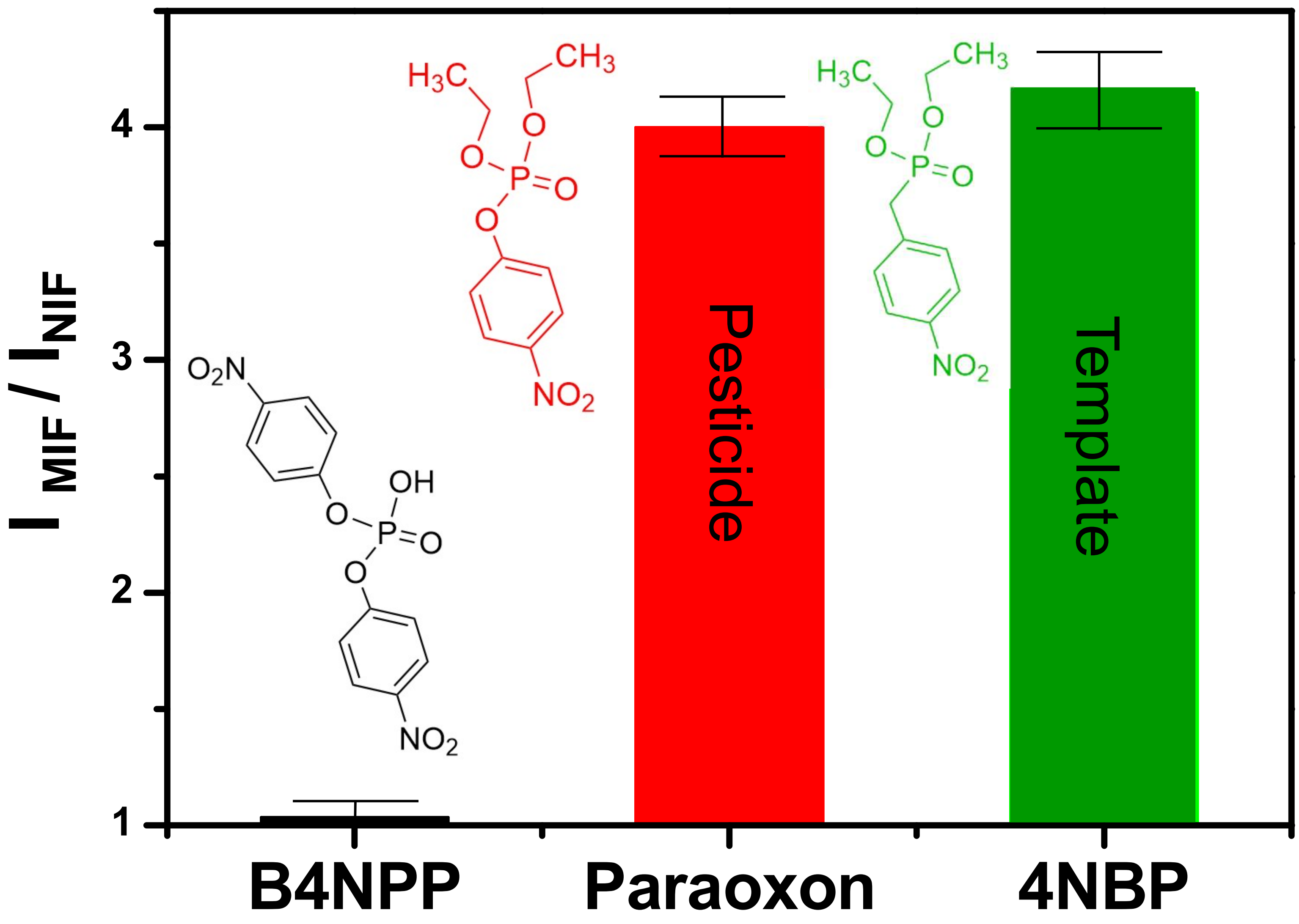
Low wettability at the ethanol droplet/active substrate interface



GERS spectra of paraoxon in water and ethanol (v/v=1:10) solution measured on imprinted substrates.

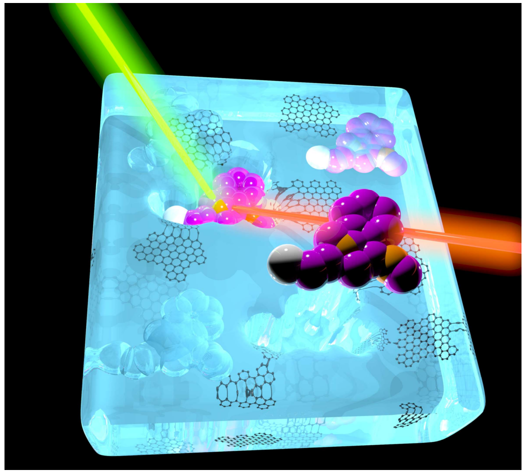
D. Carboni et al., *J. Raman Spectr.*, **2018,** 49, 189-197

Selective Paraoxon detection

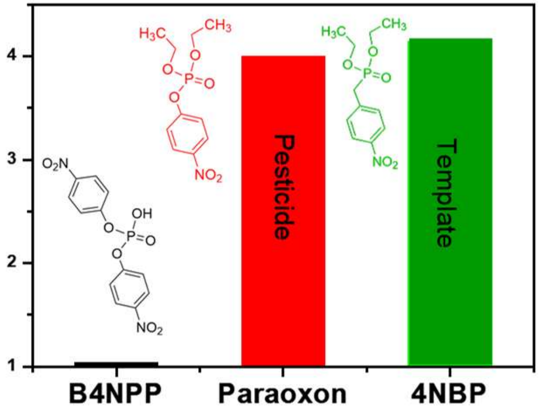


D. Carboni et al., J. Raman Spectrosc. 2018, 49, 189–197

Conclusions



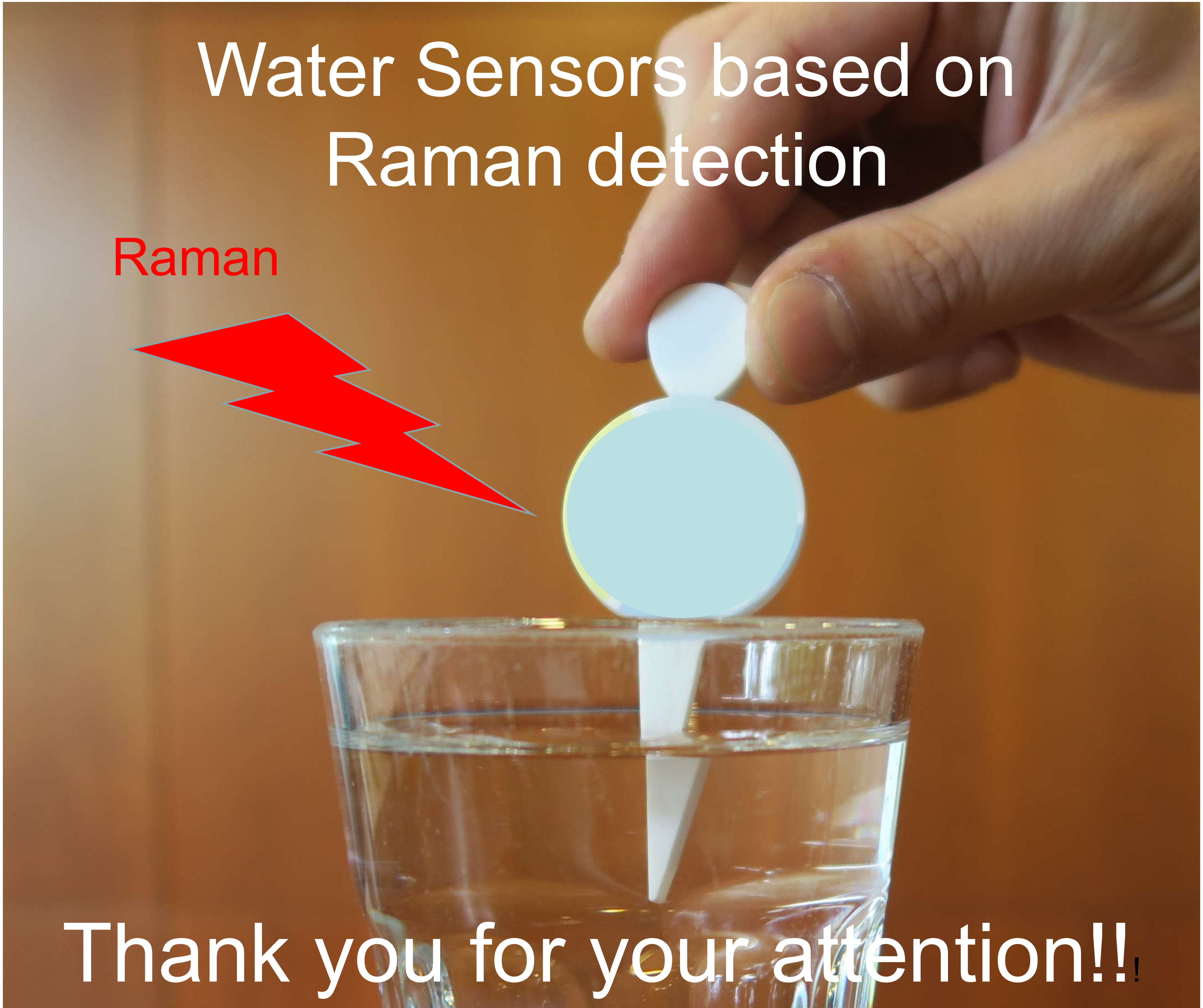
1. Hybrid porous materials incorporating physically exfoliated graphene allows synergistic effects of molecular imprinting and GERS.



2. The design of the hybrid nanocomposite can be tuned "on-demand" depending on the targeted analyte.

3. Fast, easy and reproducible environmental sensing in water can be obtained with a good detection limit.

Water Sensors based on Raman detection



Thank you for your attention!!!