

# **Tuning the surface properties of hybrid organic-inorganic nanoparticles**

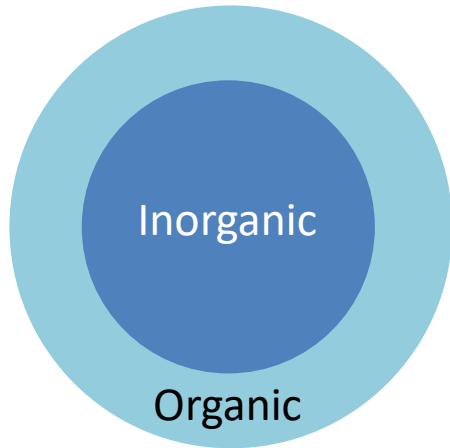
Bilateral Workshop

Nanotechnology and Nanoapplication

February 5 - 6, 2020, Ljubljana

Paolo Pengo  
University of Trieste

# The surface properties of hybrid organic-inorganic nanoparticles



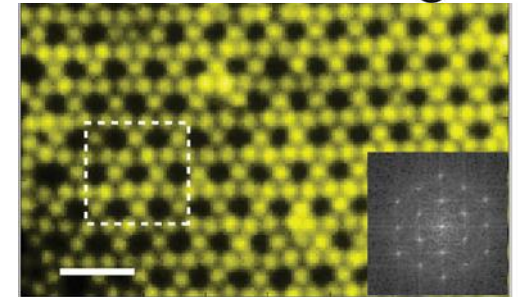
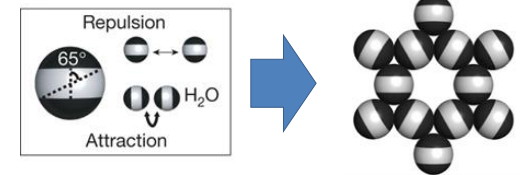
Surface Anisotropy

Solubility and stability in solution

Recognition of small molecules

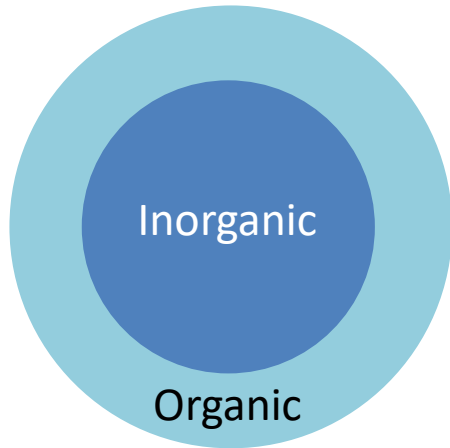
Adhesion to nano and mesostructures

Self-assembly



*Nature* **2011**, 469, 381–384

# The surface properties of hybrid organic-inorganic nanoparticles



Surface Anisotropy

Solubility and stability in solution

Recognition of small molecules

Adhesion to nano and mesostructures

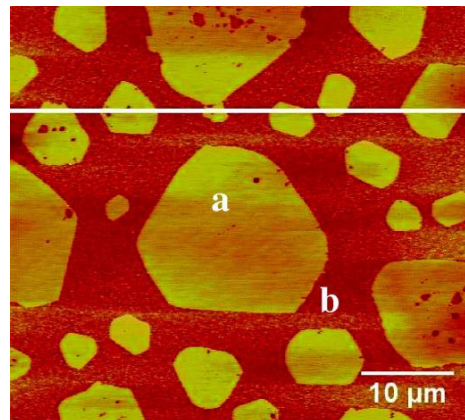
Self-assembly

Bulk



*Chem. Soc. Rev.*, **2012**,41, 31-42

Meso-scale

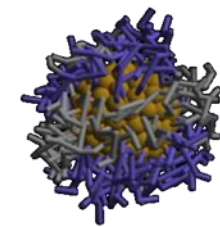
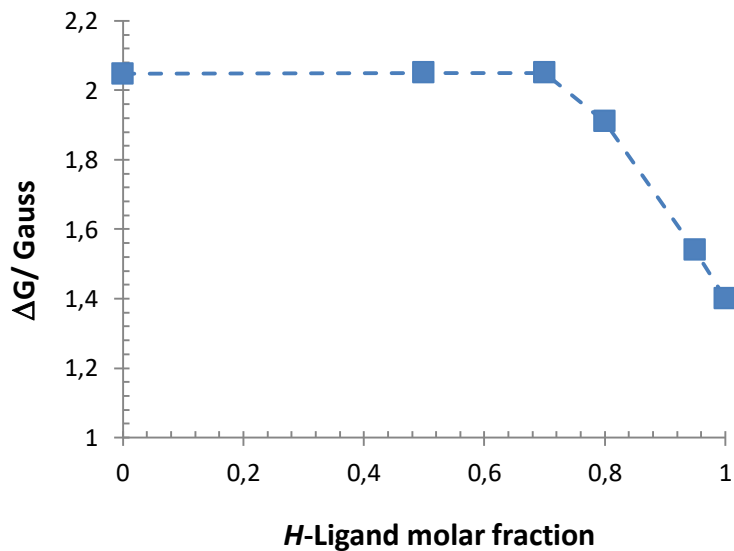
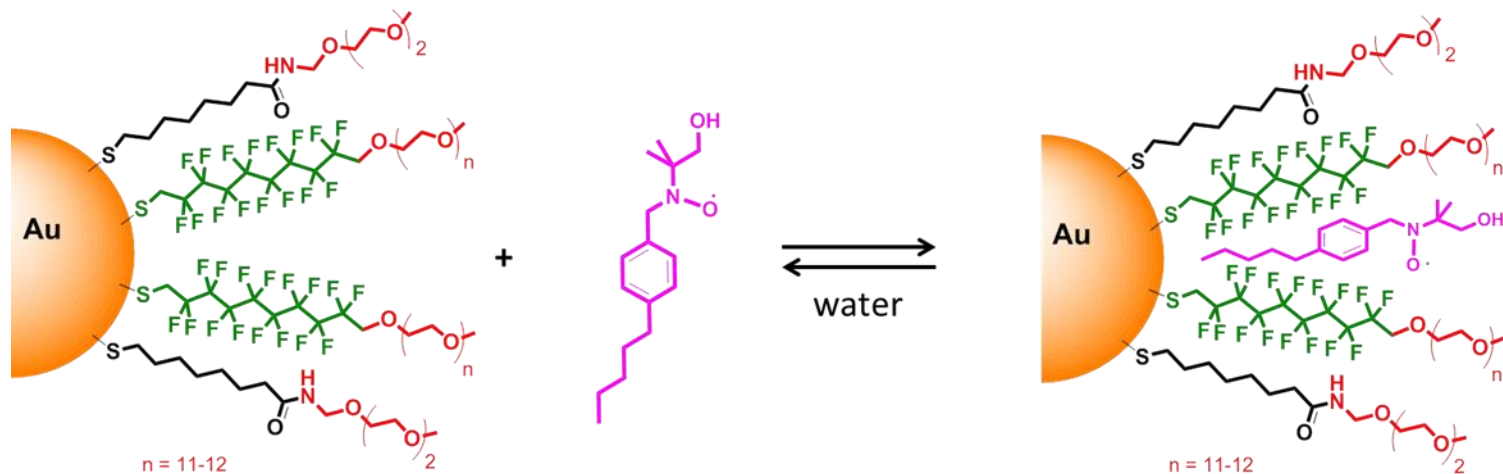


*J. Colloid Interface Sci* **2012**, 380, 105–112

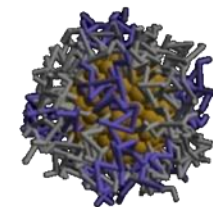
Nano-scale

?

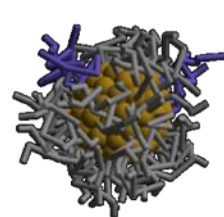
# ESR highlights discrete patches on the surface of mixed-monolayer gold nanoparticles



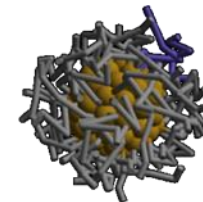
$X_H = 0.50, \varnothing 2.2 \text{ nm}$



$X_H = 0.71, \varnothing 2.5 \text{ nm}$

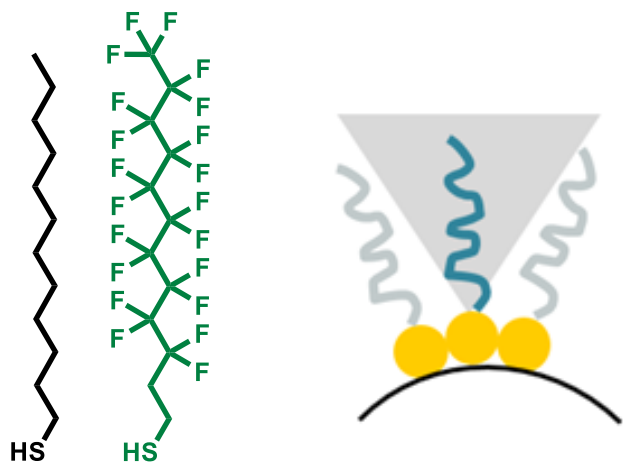


$X_H = 0.80, \varnothing 1.9 \text{ nm}$

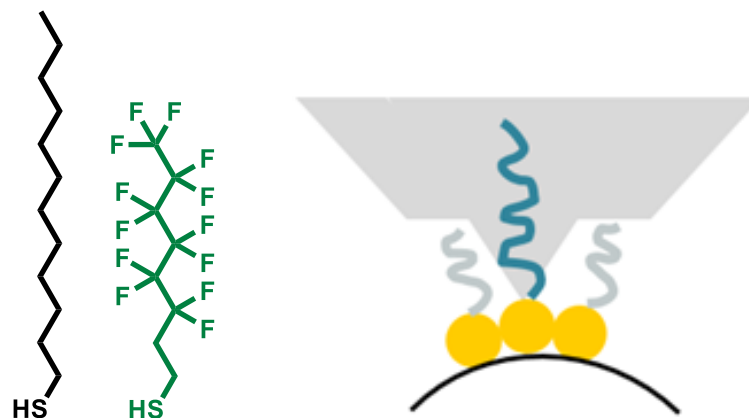


$X_H = 0.95, \varnothing 1.9 \text{ nm}$

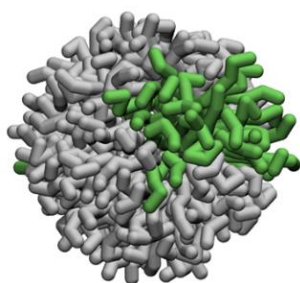
# Can we predict a monolayer morphology on a design basis? A matter of entropy-enthalpy balance and ligands structure



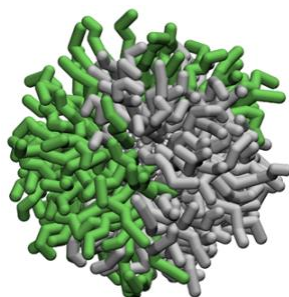
Low conformational entropy



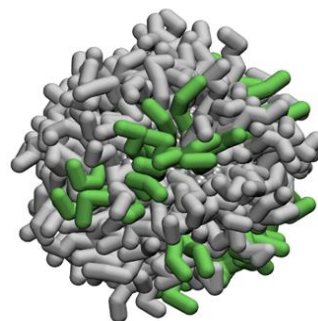
High conformational entropy



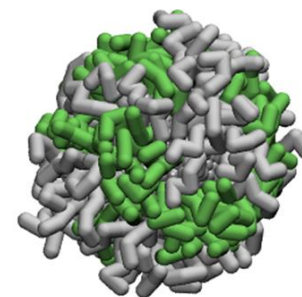
$\text{Au}_{1289}\text{C12}_{194}\text{F10}_{31}$   
13.9 % **F10**



$\text{Au}_{1289}\text{C12}_{133}\text{F10}_{88}$   
36.6 % **F10**



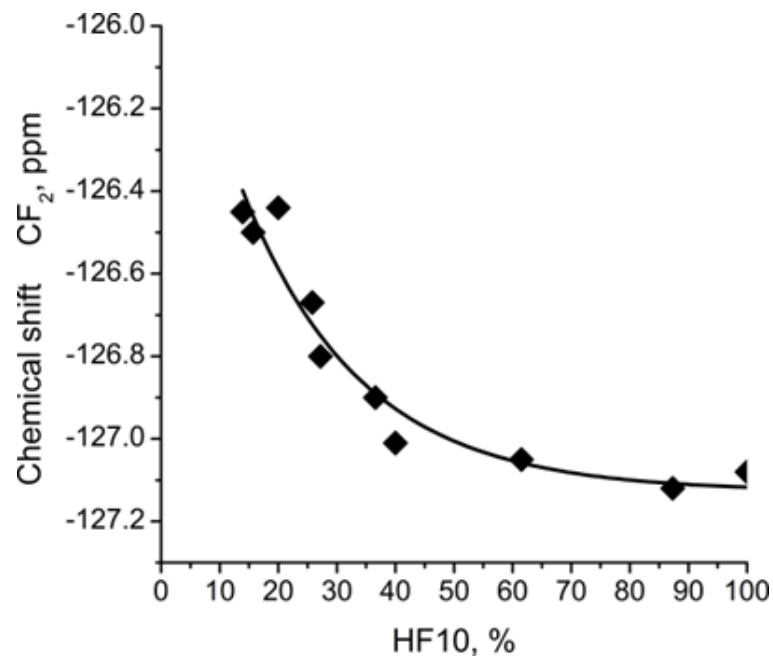
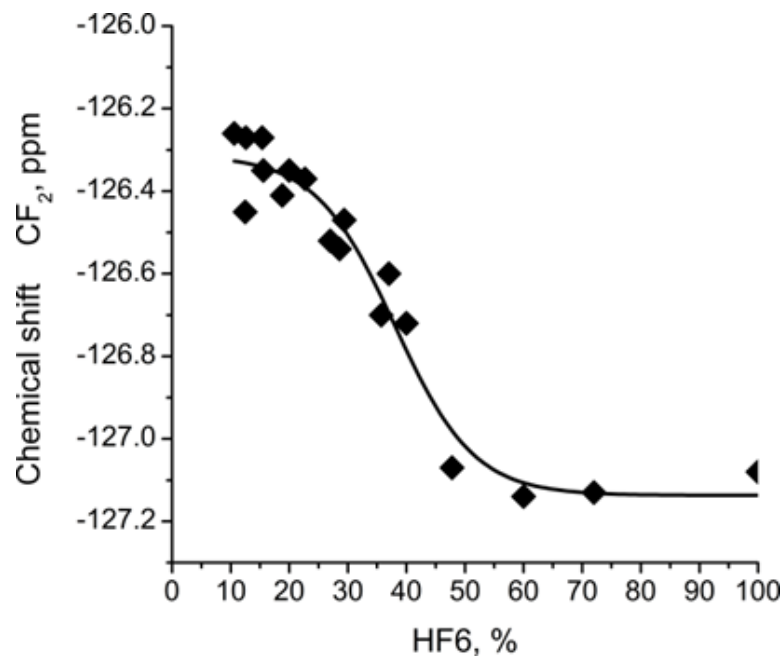
$\text{Au}_{1289}\text{C12}_{185}\text{F6}_{46}$   
20% **F6**



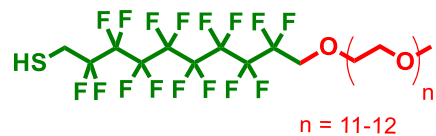
$\text{Au}_{1289}\text{C12}_{123}\text{F6}_{112}$   
47.8% **F6**

# Different morphologies have specific spectroscopic signatures

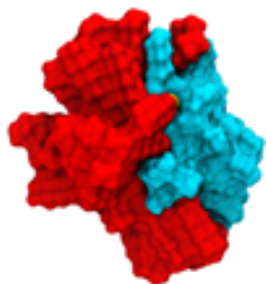
## $^{19}\text{F}$ NMR analyses



# 'monolayer isomers' have different interaction properties with phospholipid membranes

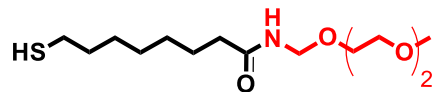


**Janus**

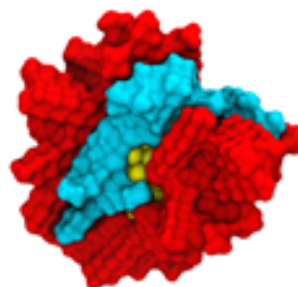


$\text{Au}_{140}\text{H}_{24}\text{F}_{32}$   $D = 1.6$  nm

$K_D = 330 \pm 50$   $\mu\text{M}$



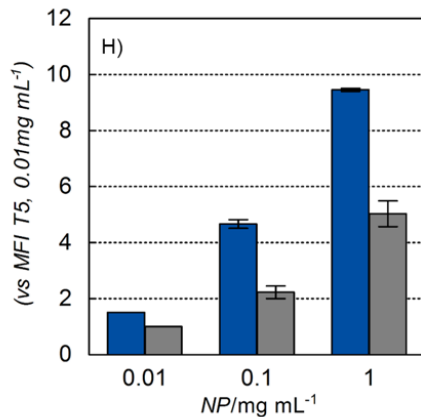
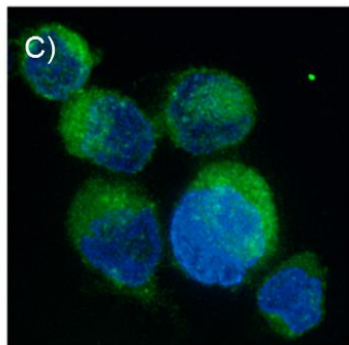
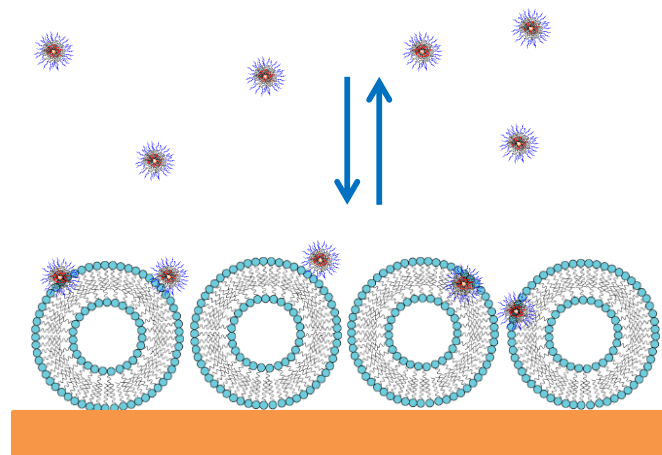
**Stripe-like**



$\text{Au}_{260}\text{H}_{20}\text{F}_{36}$   $D = 1.9$  nm

$K_D = 80 \pm 30$   $\mu\text{M}$

Probing nanoparticles-membrane interaction  
*via* SPR



Morphology	$\Delta G_{adh}$ [Kcal/mol]	N° contacts	Contacts	
			Hydrophylic [%]	Hydrophobic [%]
Janus	$-28.6 \pm 1.5$	$21 \pm 2$	59	41
Stripe-like	$-38.9 \pm 1.0$	$25 \pm 1$	63	37

# Conclusions and Perspectives

Different monolayer morphologies are predictable because encoded in the structures of the passivating ligands

Different monolayer morphologies are addressable by spectroscopic techniques

Tuning the monolayer morphology allows endowing particles with different interaction properties

We are interested in exploiting these materials in the biomedical field and material sciences



# Acknowledgments

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UNIVERSITÀ  
DEGLI STUDI DI TRIESTE



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MINISTERO DELL' ISTRUZIONE, DELL'UNIVERSITÀ E DELLA RICERCA