



# CNR-NAST Meeting (22/06/2009)

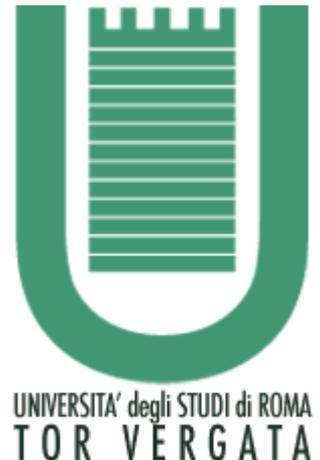
## *Bio-hybrid Materials: matching Soft and Hard Matter*

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*venanzi@uniroma2.it*

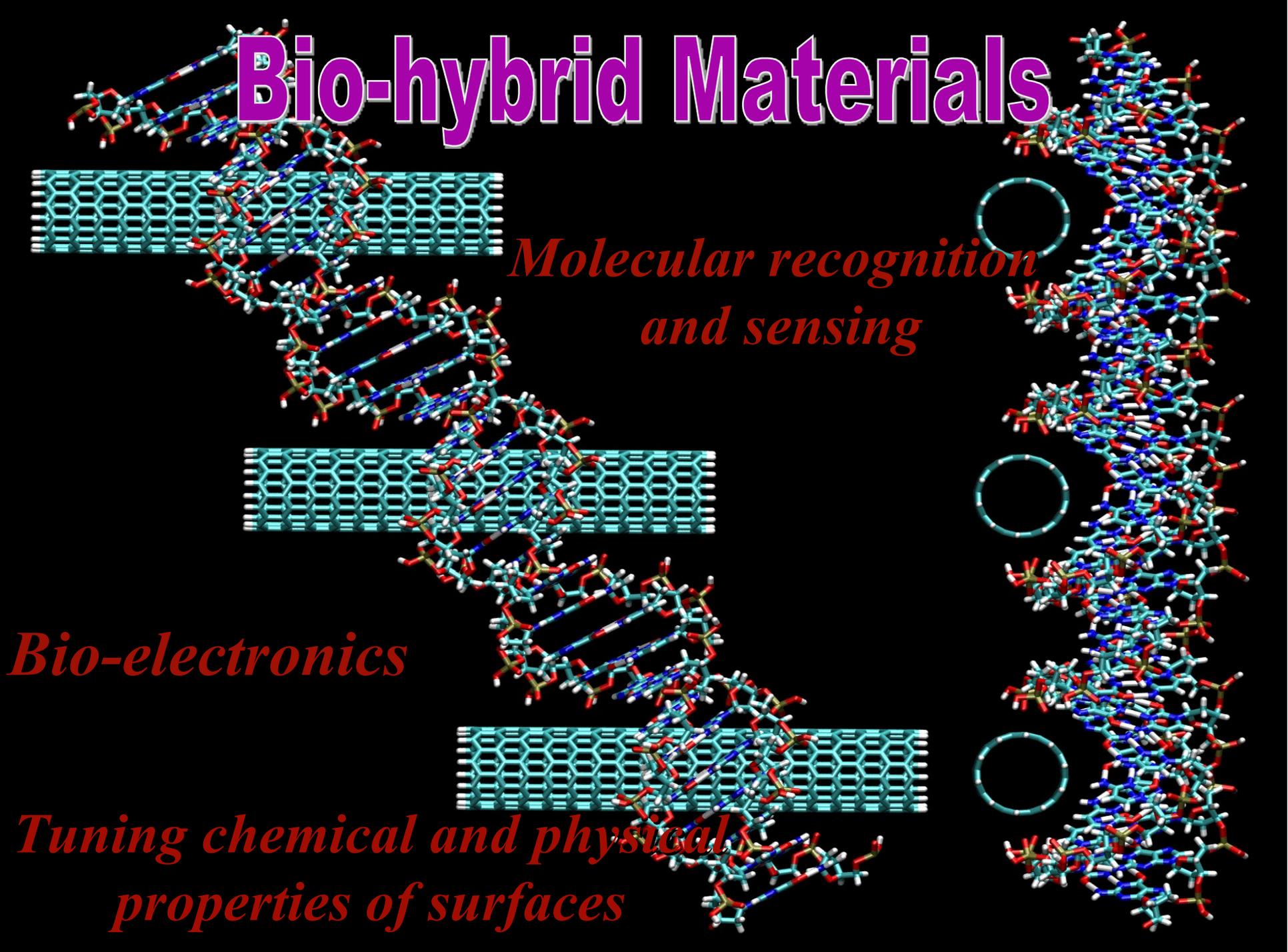


**Nanoscienze & Nanotecnologie & Strumentazione**

CENTRO INTERDIPARTIMENTALE  
UNIVERSITÀ DEGLI STUDI DI ROMA TOR VERGATA



# Bio-hybrid Materials



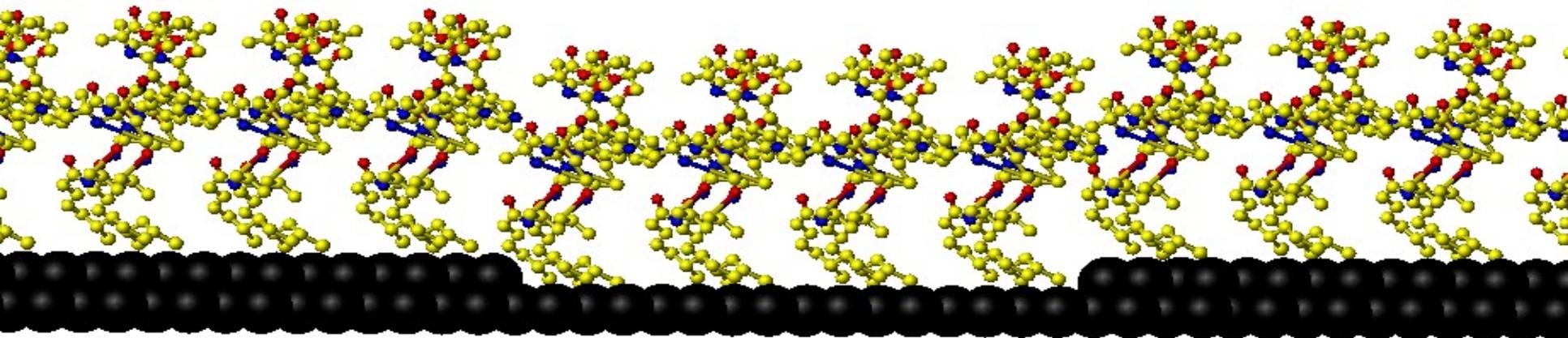
*Molecular recognition  
and sensing*

*Bio-electronics*

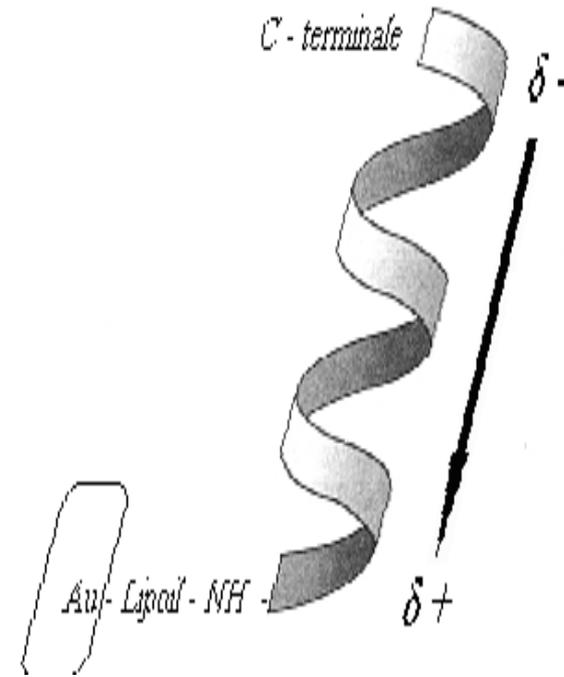
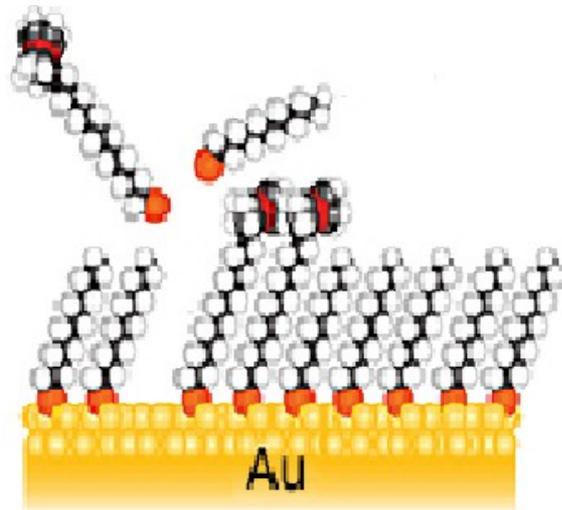
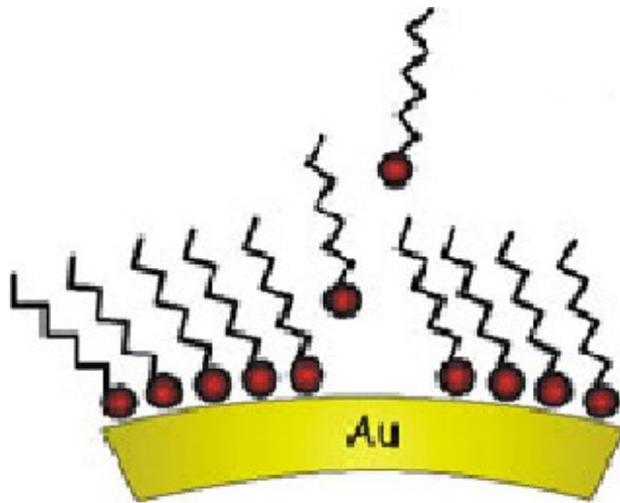
*Tuning chemical and physical  
properties of surfaces*

# Outline

- *Peptide-based SAMs*
- *Supported Phospholipids*
- *Mesoscopic aggregates of chiral porphyrins*

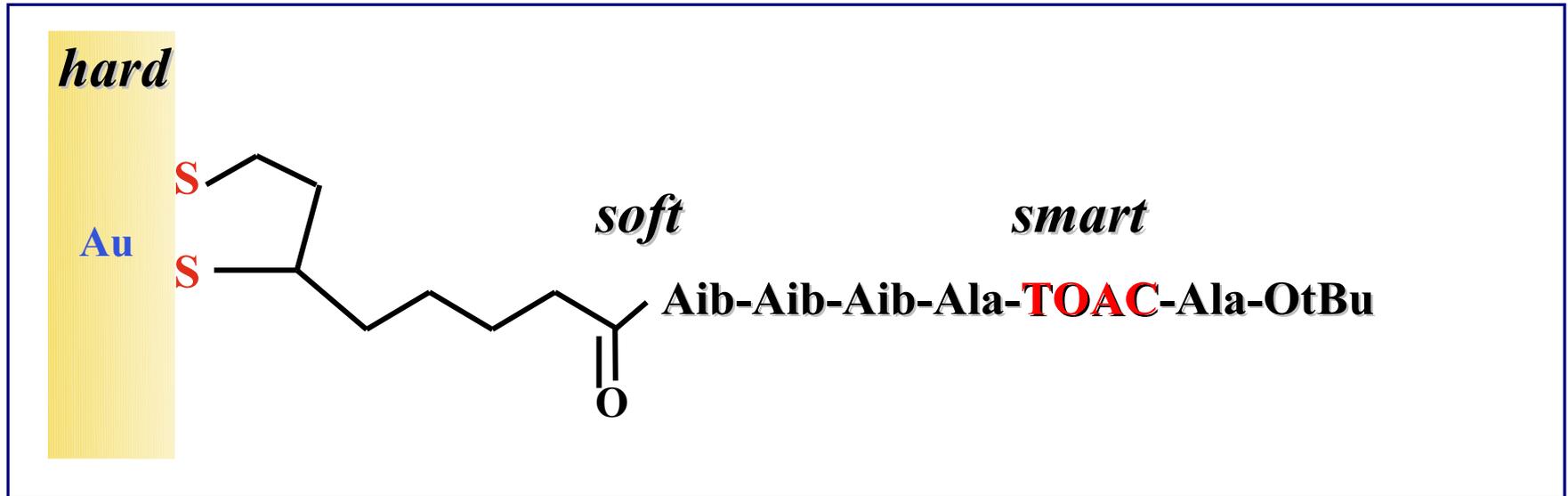


# Peptide Self-Assembled Monolayers



***Helical peptides forms densely-packed and structurally ordered SAMs***

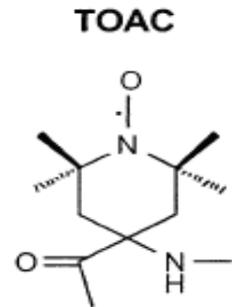
# Electron Transfer through a peptide SAM



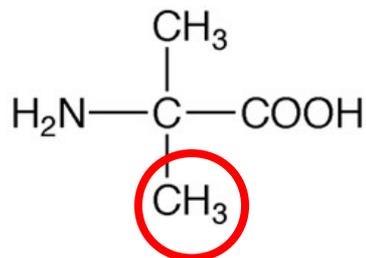
➤ *N-terminal lipoic group (disulfide binding on Au)*

➤ *3<sub>10</sub>-helix (Aib-rich peptide)*

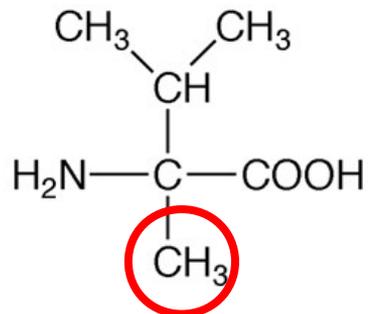
➤ *functionalized with an electroactive group (TOAC) for ET studies*



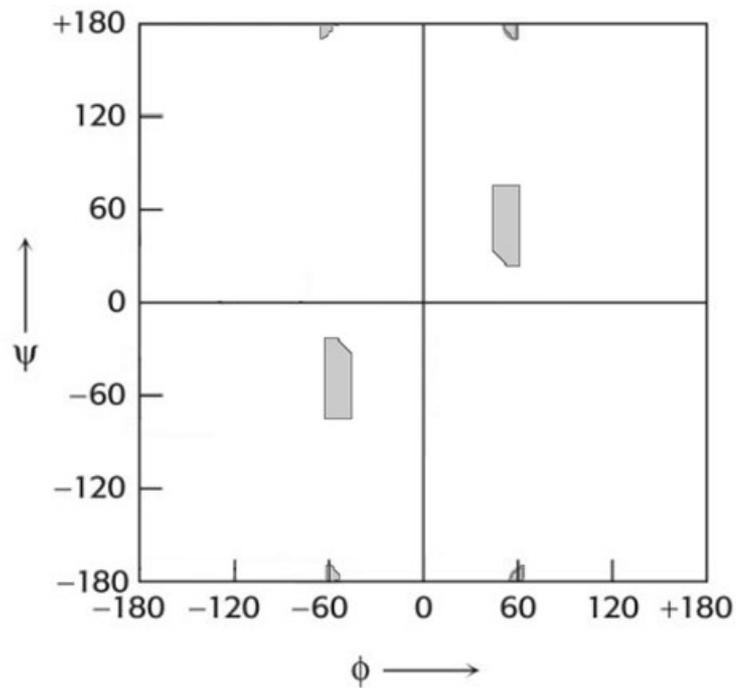
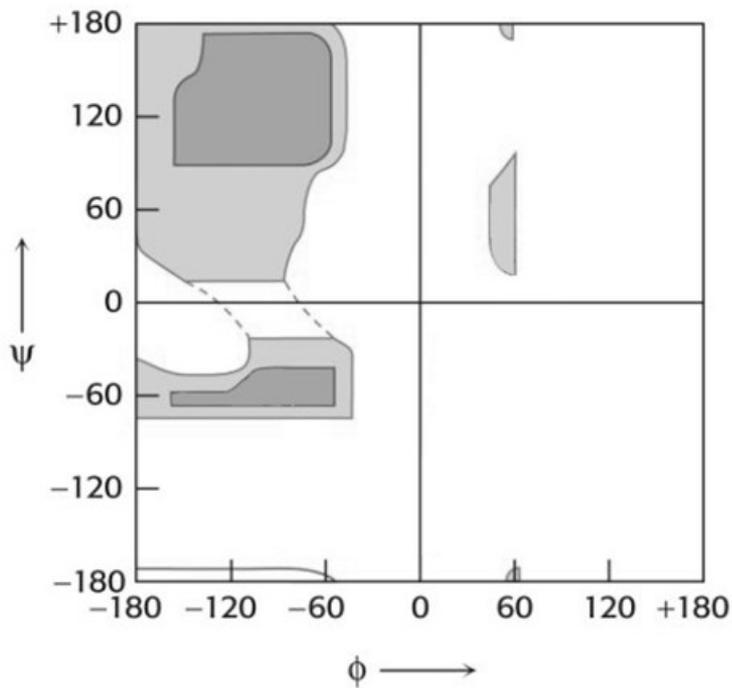
# ***C<sup>α</sup> tetrasubstituted aminoacids***



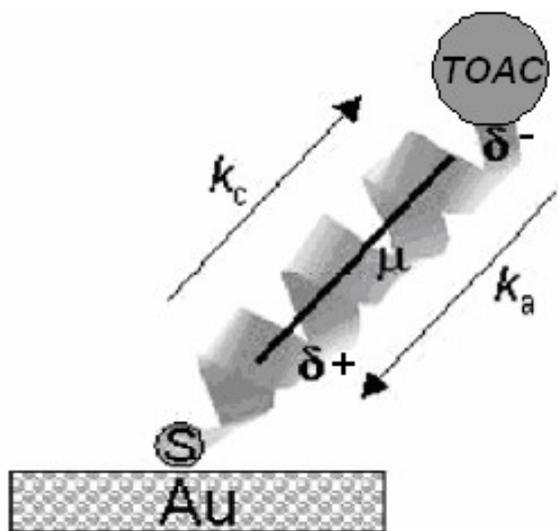
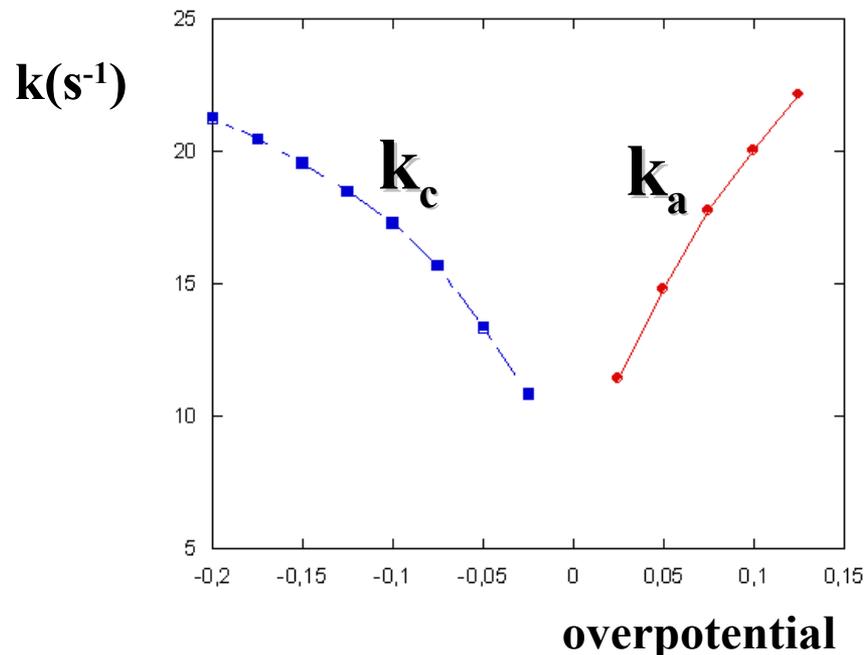
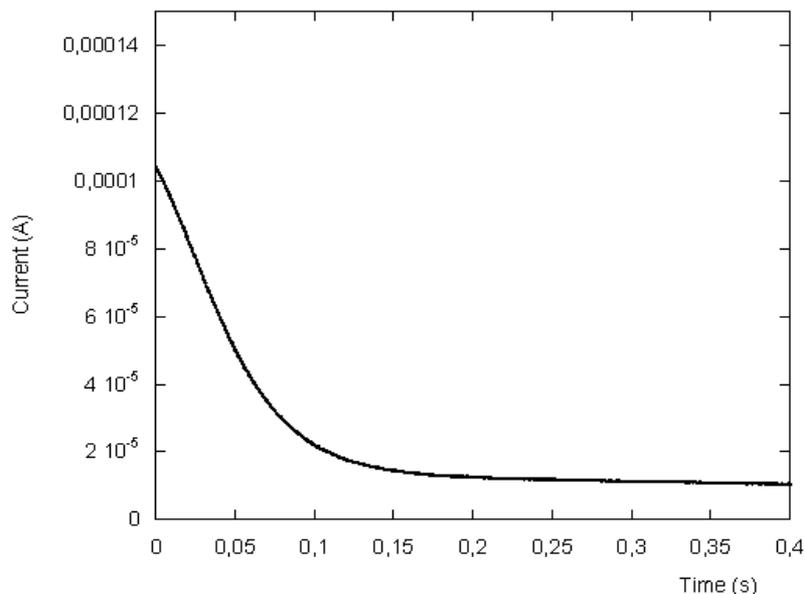
**Aib**



**( $\alpha$ Me)Val**



# *Electron Transfer through a peptide SAM*

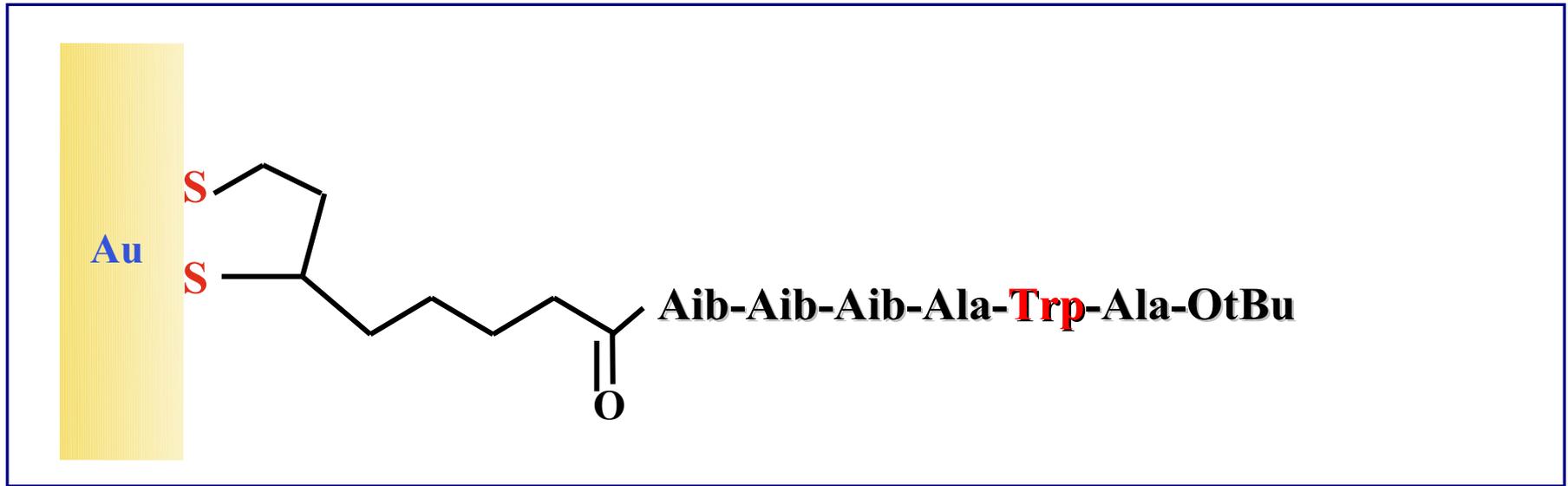


*The ET rate constant vs.  $V$  behaviour is affected by the helix dipole electrostatics*

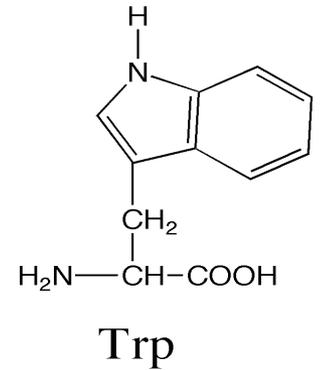
*J. Pept. Sci. 14 (2008) 184*

*Special Issue: Peptides in Nanotechnology*

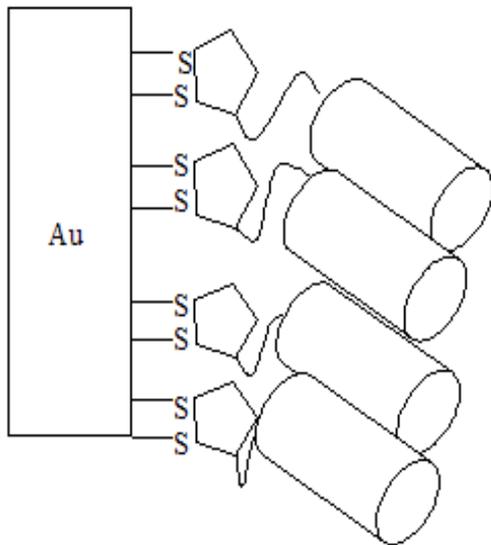
# Photoinduced ET through a peptide SAM



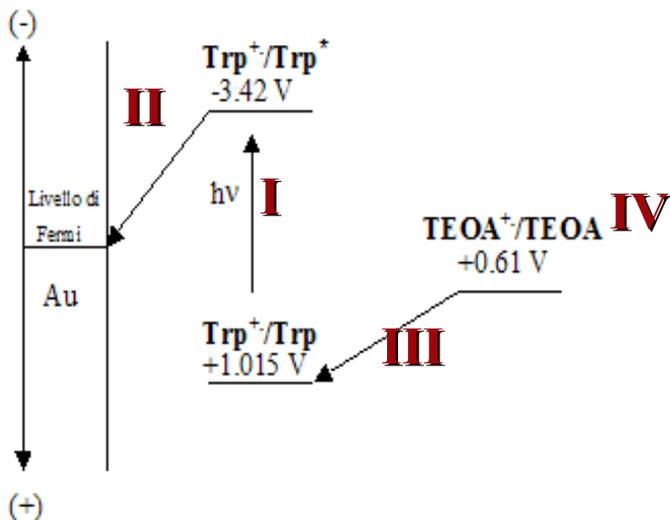
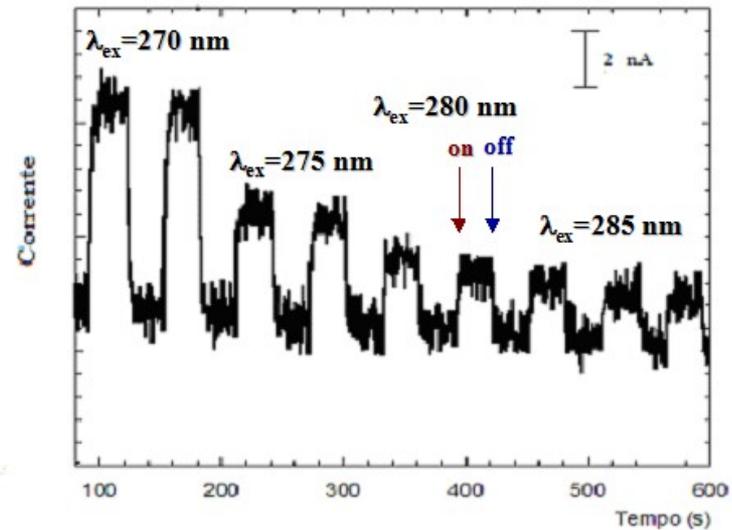
- *N-terminal lipoic group (chemisorption on gold)*
- *$3_{10}$ -helix structure*
- *Trp is an antenna group, strongly absorbing in the UV region*



# The antenna effect: Anodic Photocurrent



**TEOA**  
(Electron donor)



**I** – Photoexcitation

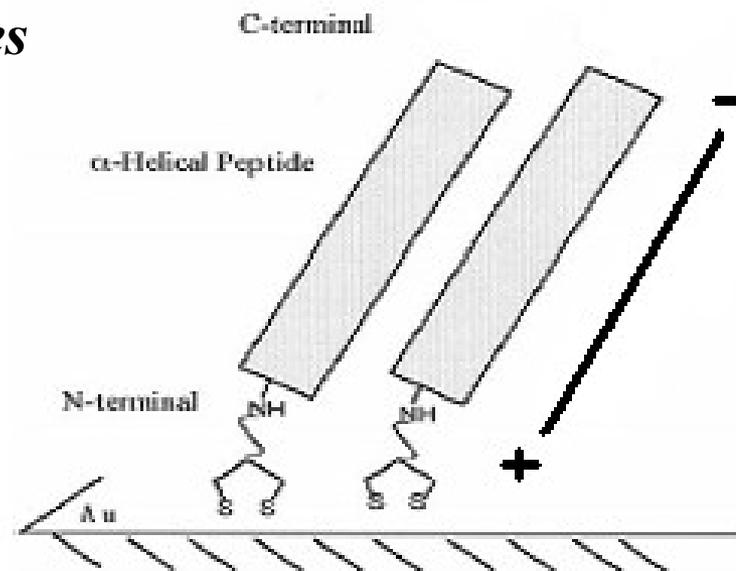
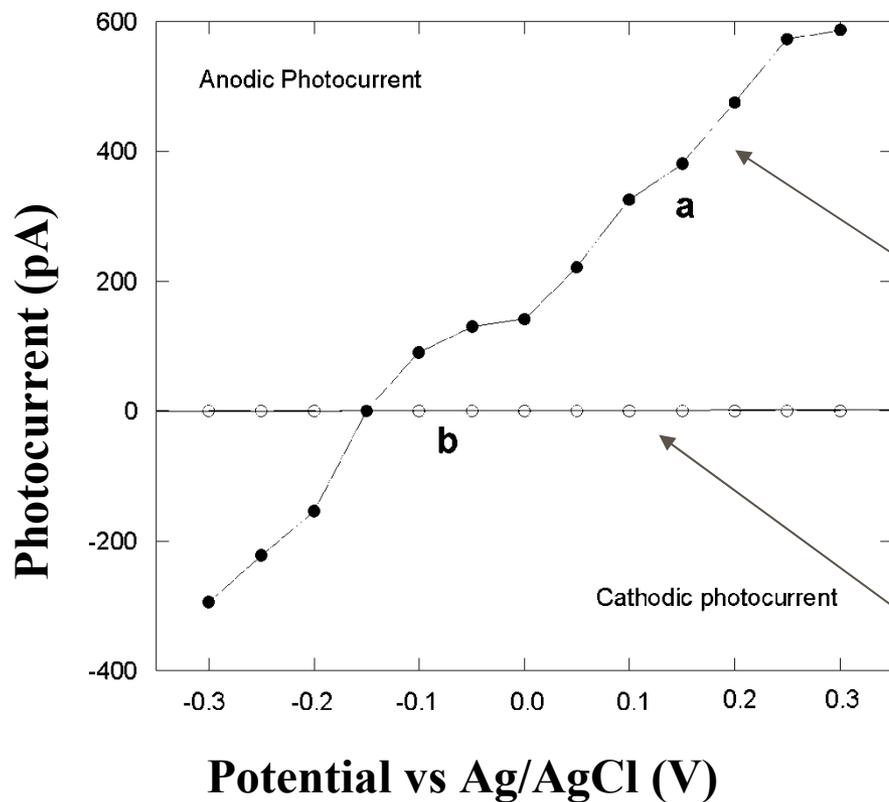
**II** –  $\text{Trp}^* \rightarrow \text{Au ET}$

(Charge injection)

**III** –  $\text{TEOA} \rightarrow \text{Trp}^+ \text{ ET}$

**IV** –  $\text{TEOA}^+$  diffusion to the cathode

*The deposition of the peptide SAM modifies the electrochemical properties at the electrode/film interface.*



*Peptide SAM*

*Undecanethiol SAM*

# Fluorescence studies on peptide-based SAMs

*Lipo-(Aib)<sub>6</sub>-NH-CH<sub>2</sub>-Pyr*

*SSA6Pyr*

*Lipo-(Aib)<sub>6</sub>-OtBu*

*SSA6*

*Lipo-(Aib)<sub>4</sub>-Trp-Aib-OtBu*

*SSA4WA*

*Z-Aib-Api(Pyr)-L-( $\alpha$ Me)Nva-Aib-*

*(( $\alpha$ Me)Nva)<sub>2</sub>-Aib-Api(Boc)-NHtBu* *A8Pyr*

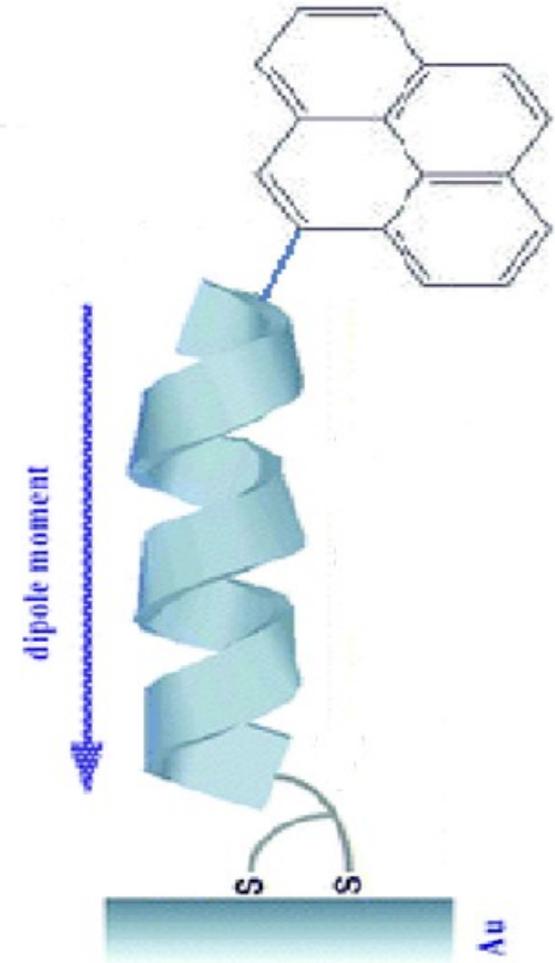
## Mono- and bi-component peptide SAMs:

SSA6Pyr

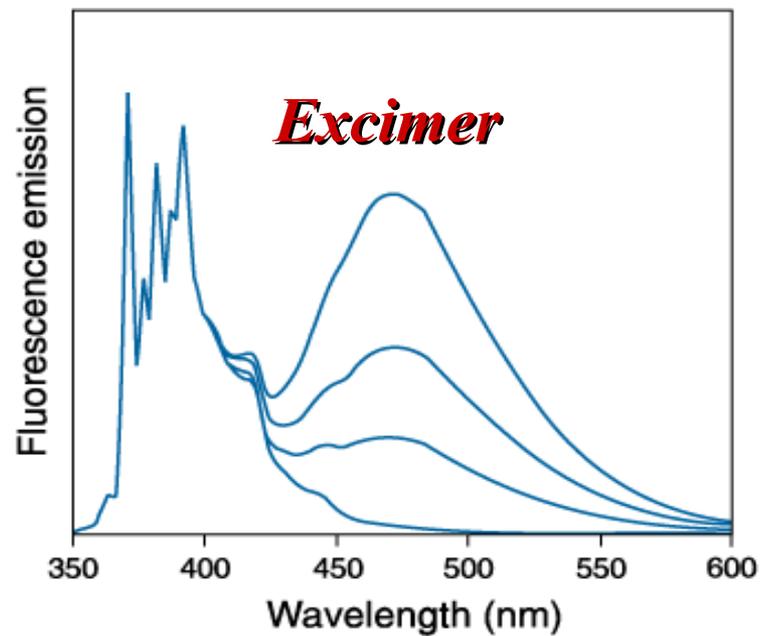
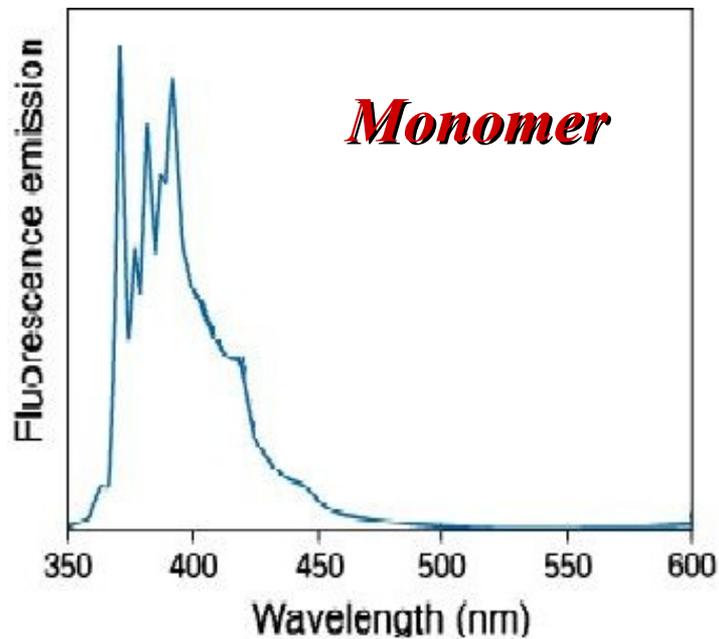
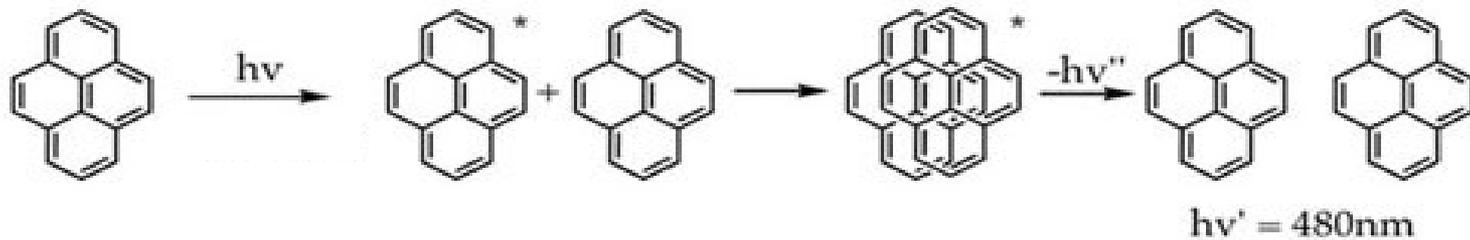
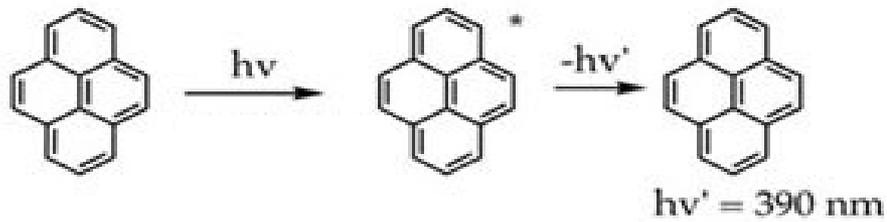
SSA6Pyr/SSA6

SSA6Pyr/SSA4WA

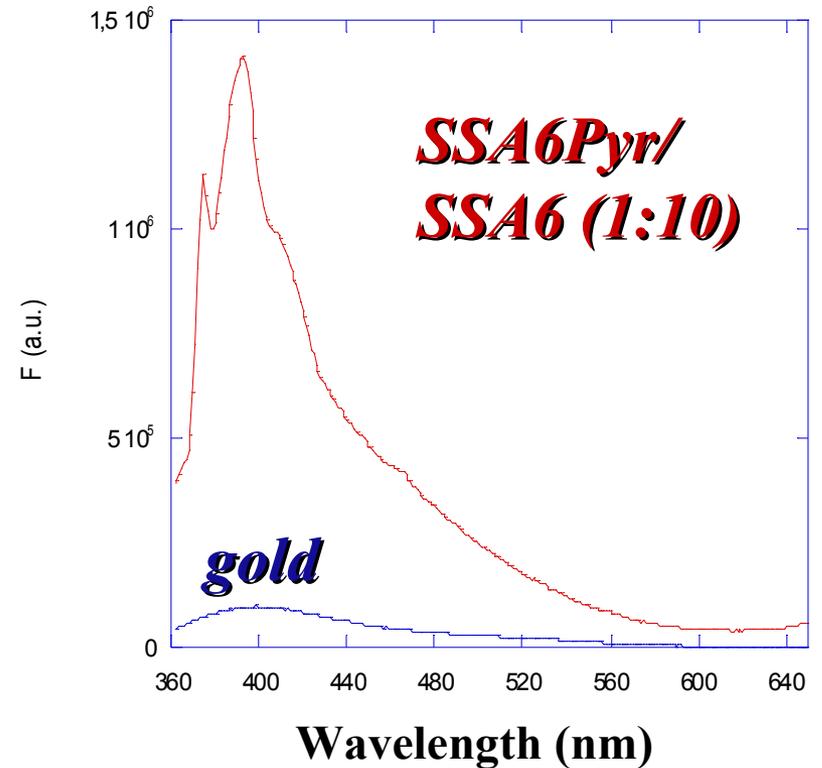
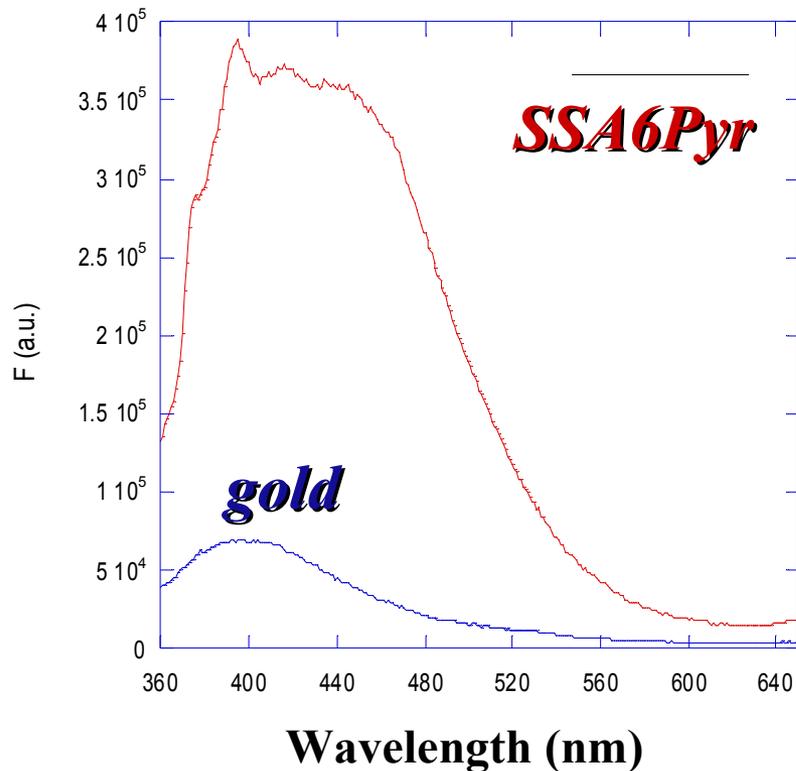
A8Pyr/SSA6



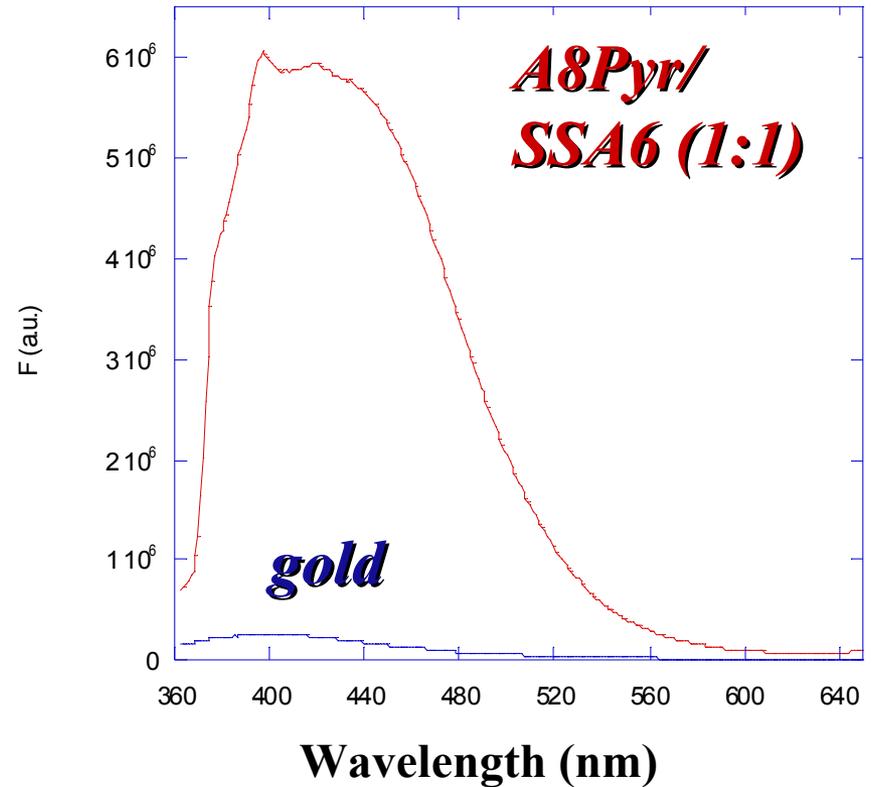
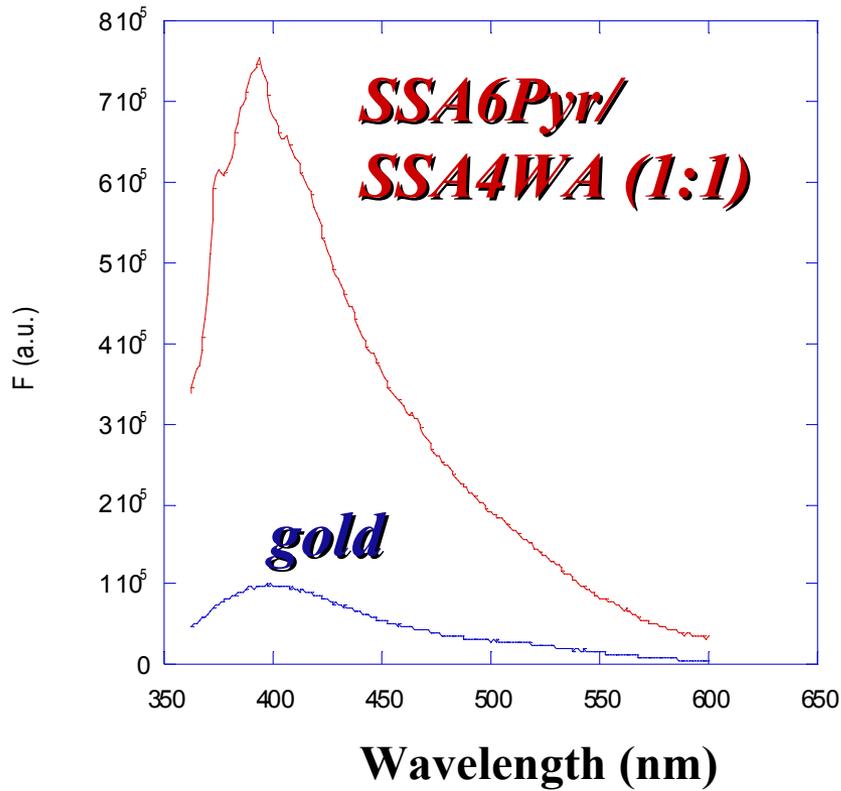
# Pyrene fluorescence in solution



# Peptide SAMs on glass-gold substrates

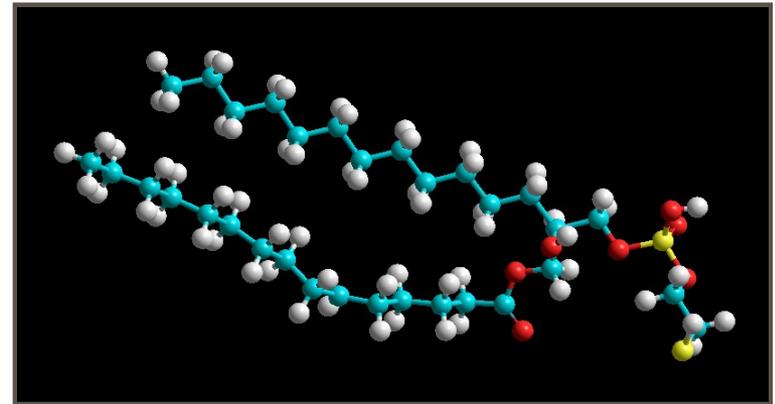
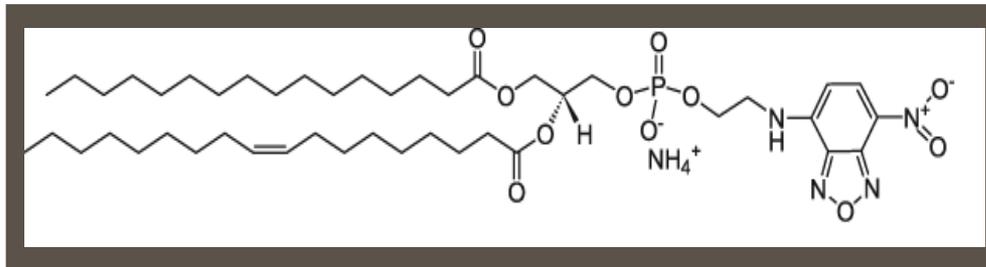


*Pyrene-Pyrene interactions stabilize the peptide SAM!*

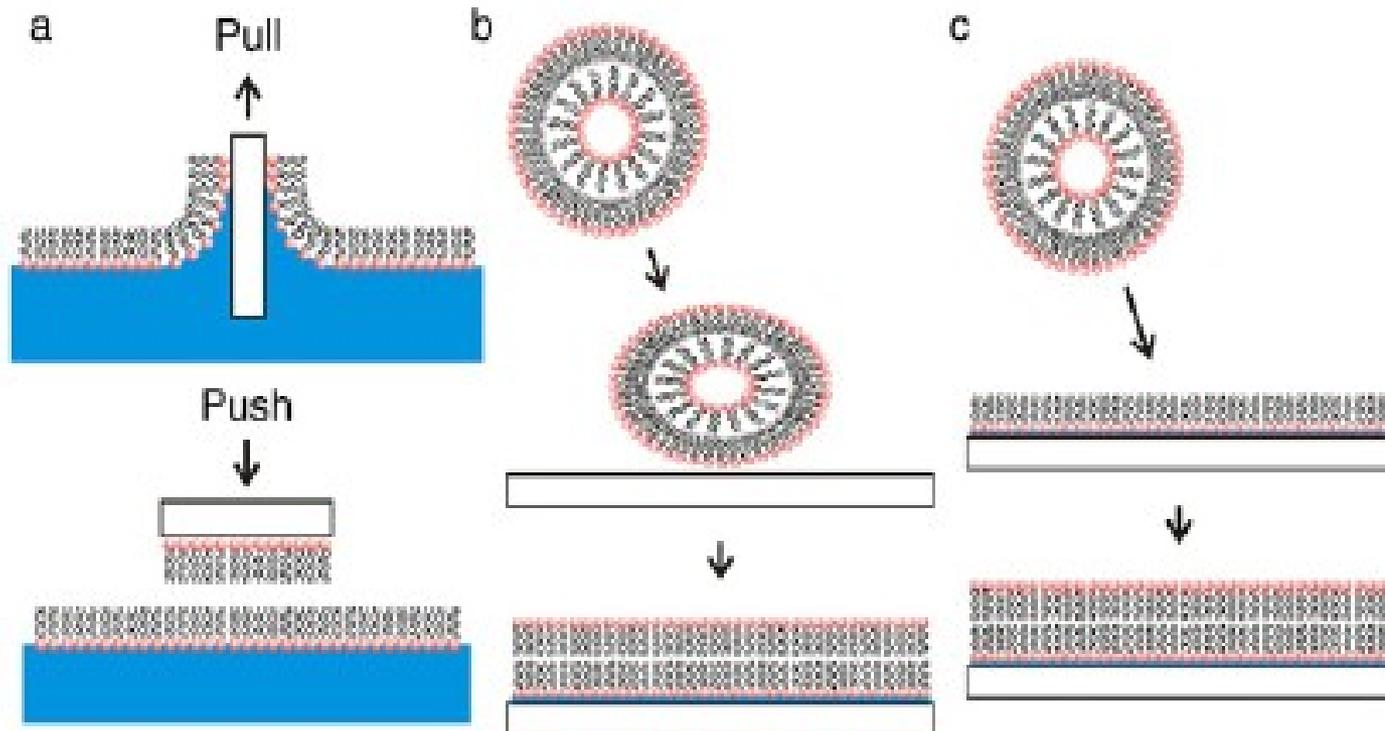


***Excimer emission reveals the formation of A8Pyr domains in the bicomponent peptide SAM!***

# Supported Phospholipids



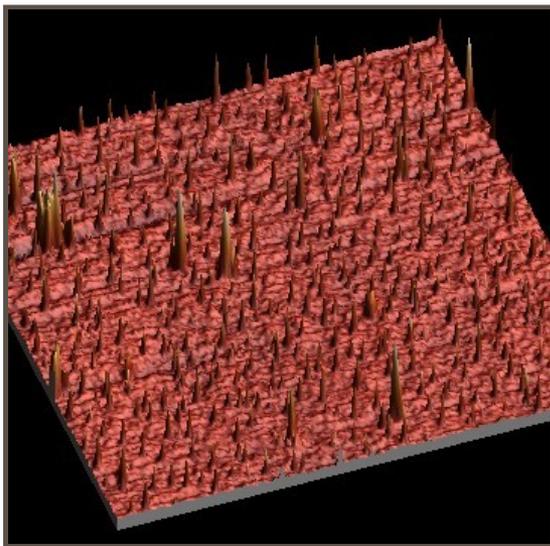
***POPC/NBD***



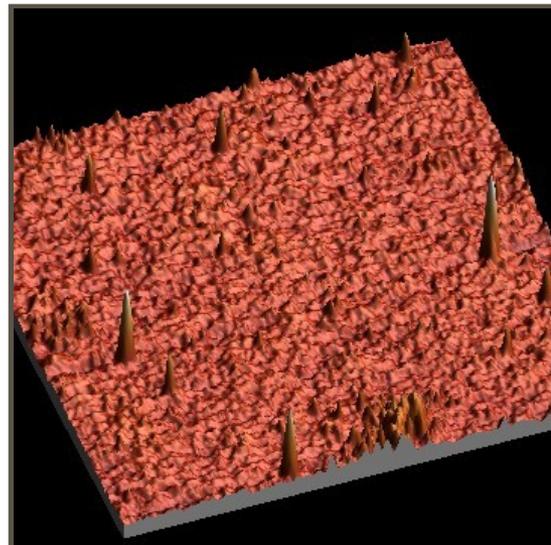


# AFM of phospholipids on glass

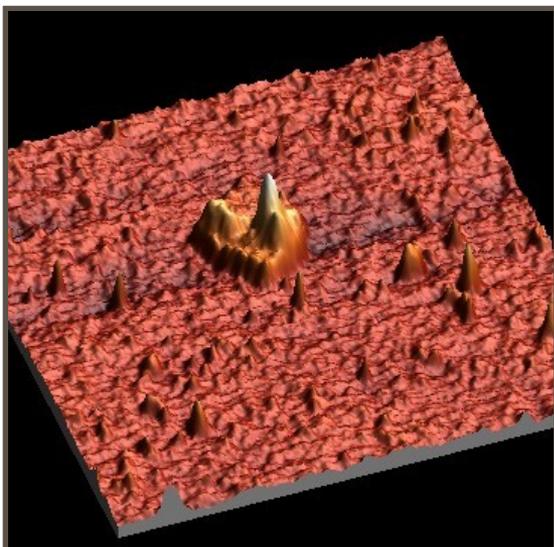
*glass*



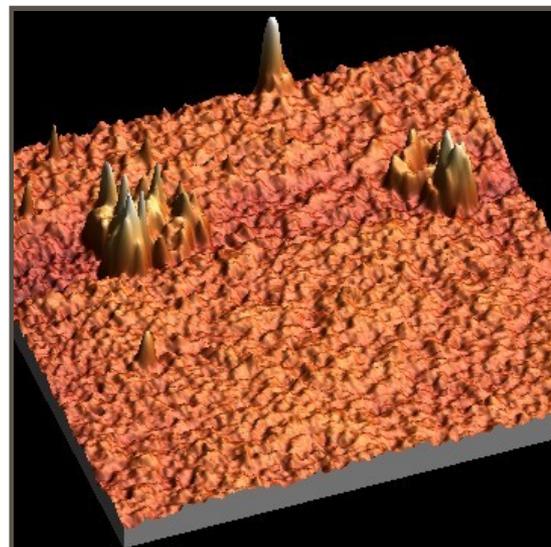
*glass*  
+  
*mono*  
*LB*



*glass*  
+  
*liposo*  
*mes*

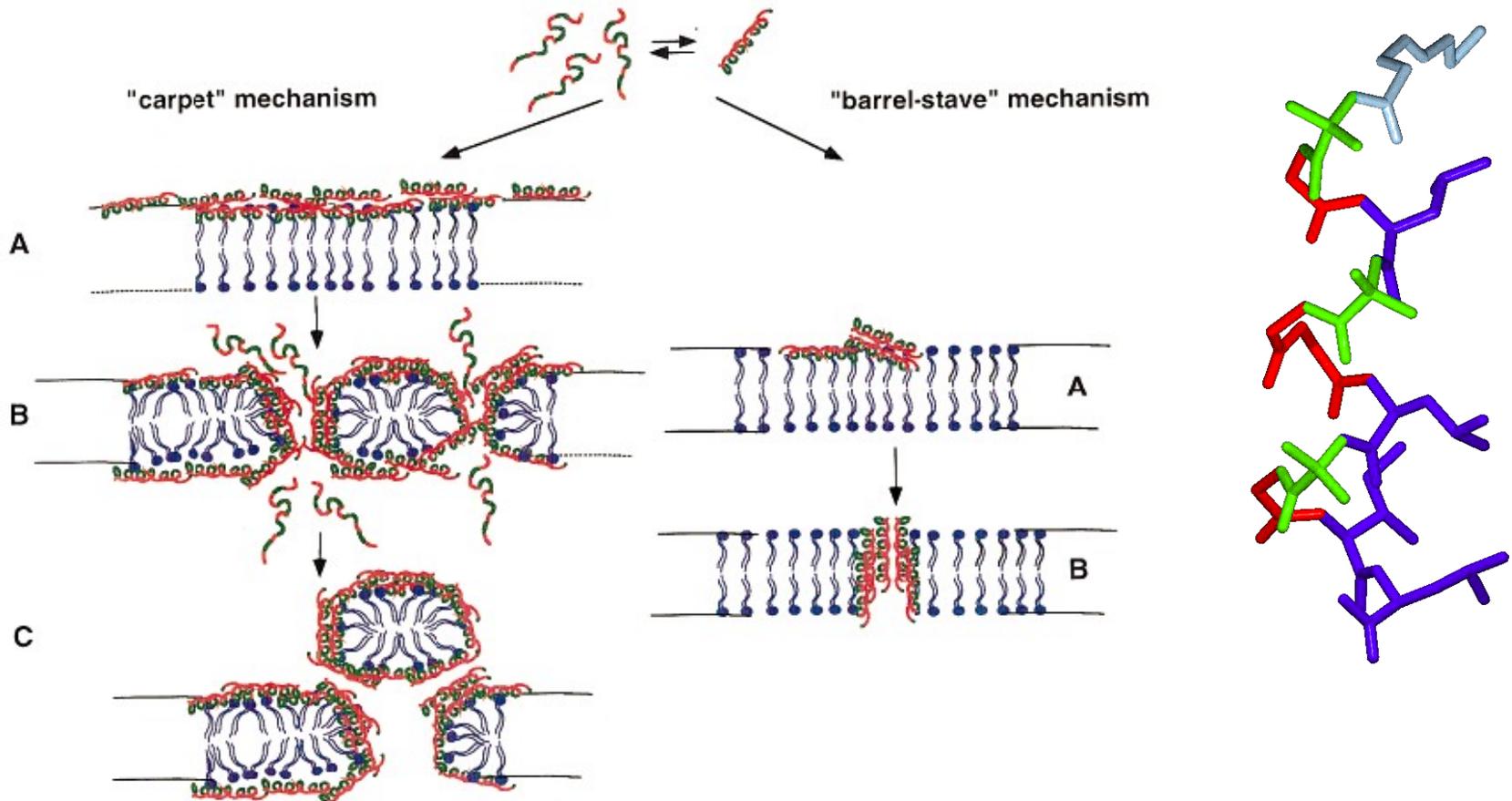


*Glass*  
+  
*mono*  
*LB*  
+  
*liposo*  
*mes*



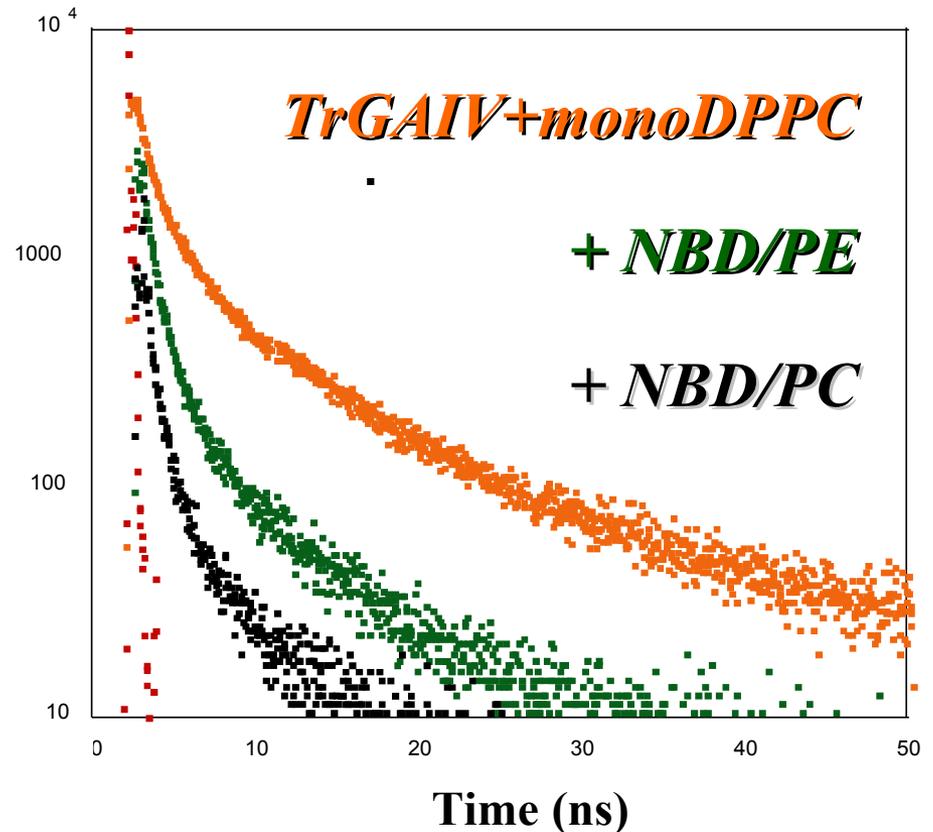
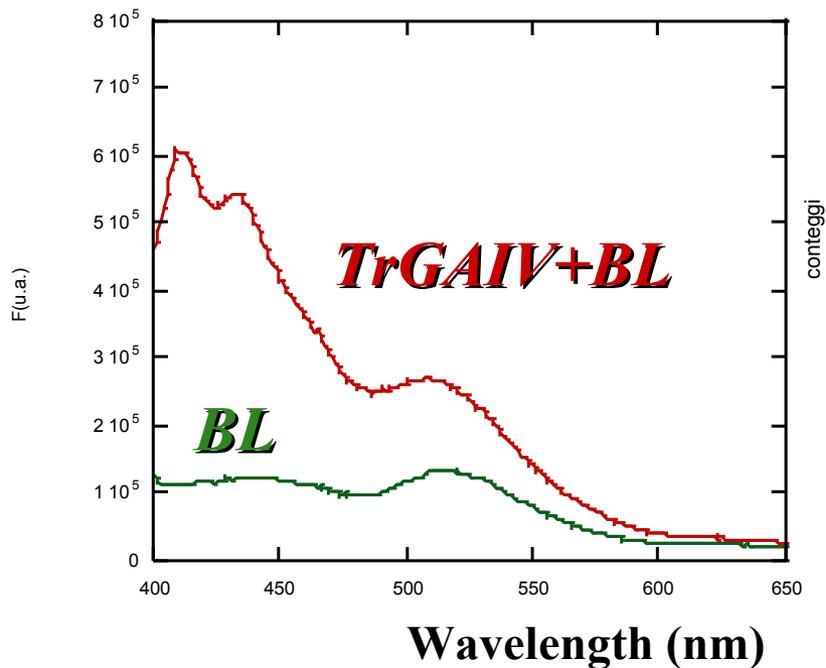
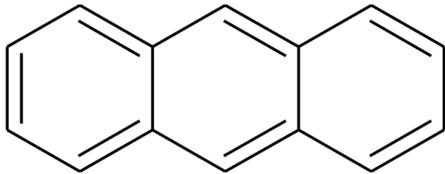
# Antimicrobial peptides: Trichogin GA IV

*Oct-Aib-Gly-Leu-Aib-Gly-Gly-Leu-Aib-Gly-Ile-Lol*

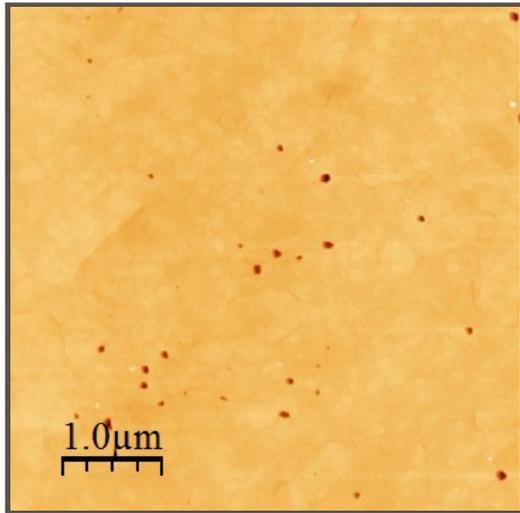


# Inclusion of Trichogin GA IV in the phospholipid layer

*Boc-AntAib-Gly-Leu-Aib-Gly-Gly-Leu-Aib-Gly-Ile-Leu-OMe*

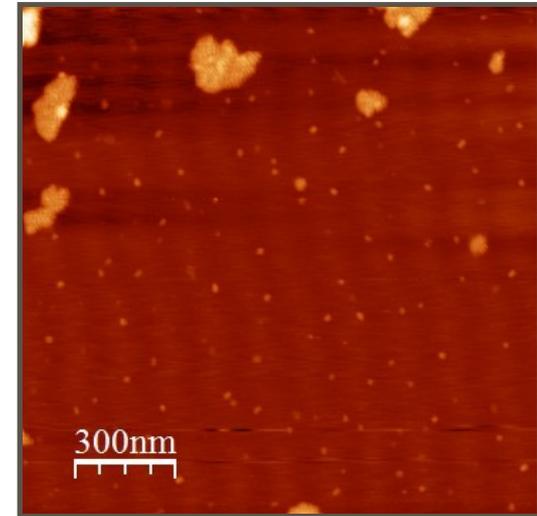


# AFM of thiophospholipids on gold + TrGAIV



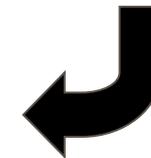
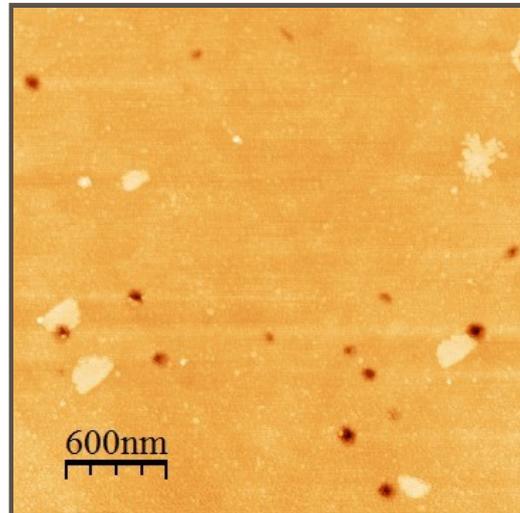
Gold 5.0 μm x 5.0 μm

deposition



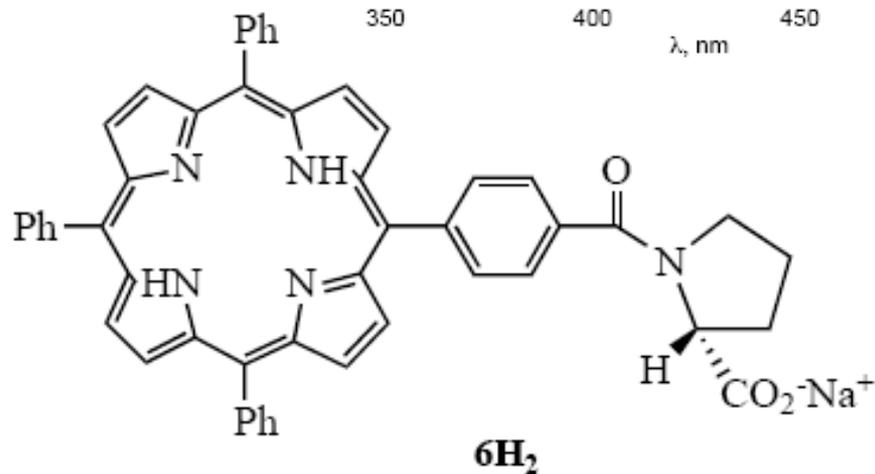
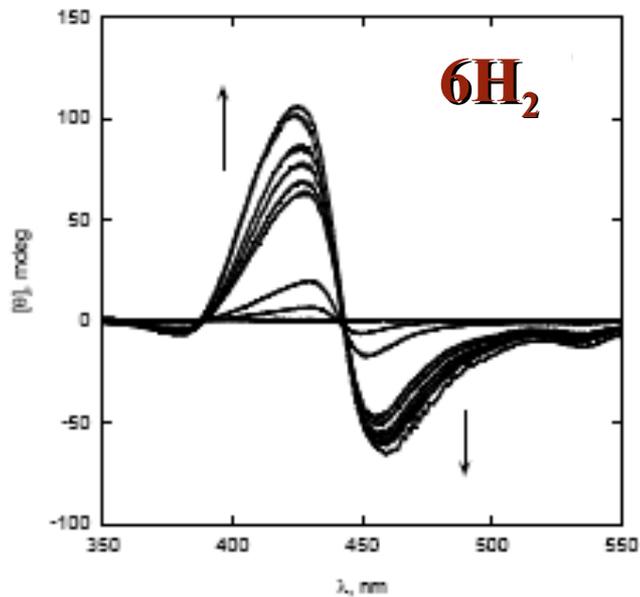
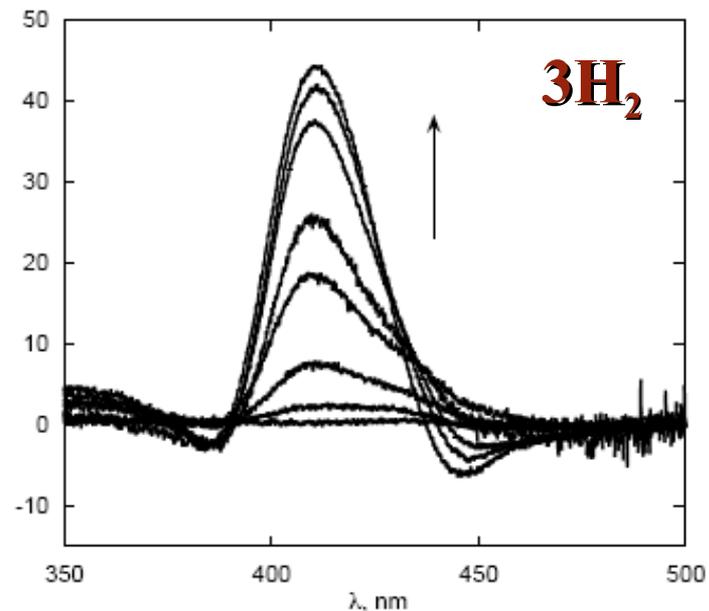
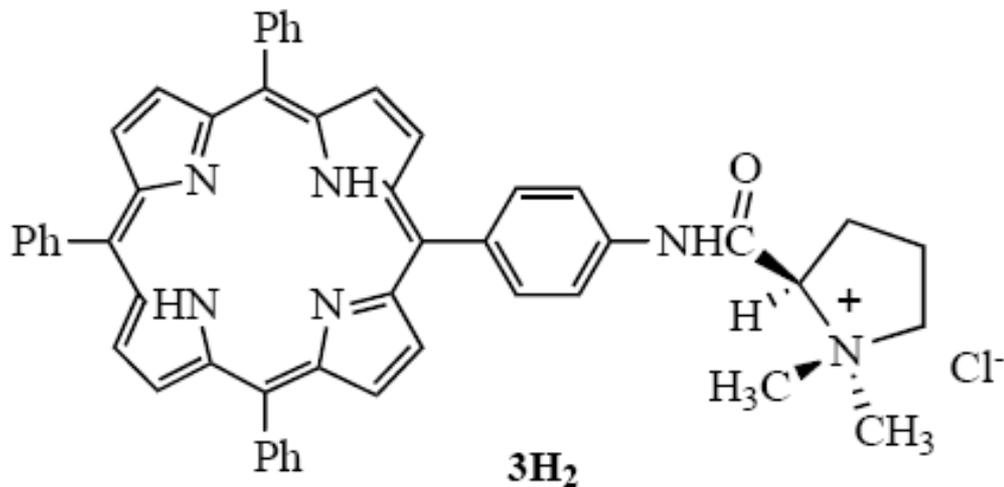
PE-SH 1.5 μm x 1.5 μm

PE-SH + TrGAIV  
3.0 μm x 3.0 μm

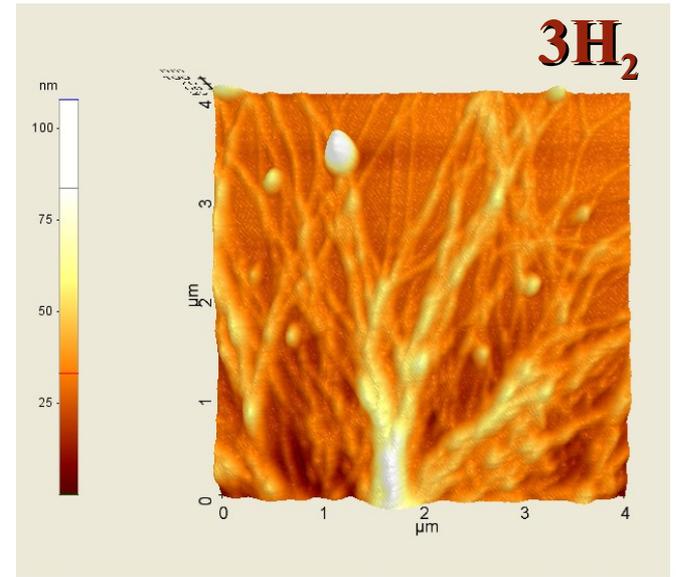
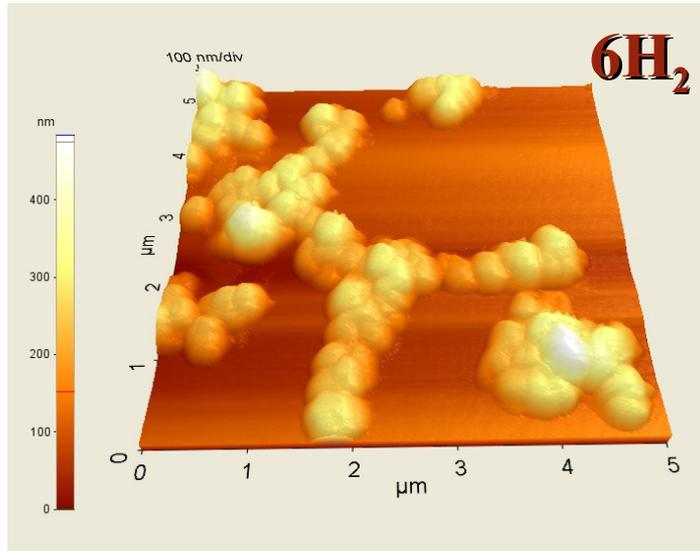


TrGAIV

# Mesoscopic aggregates of chiral porphyrins

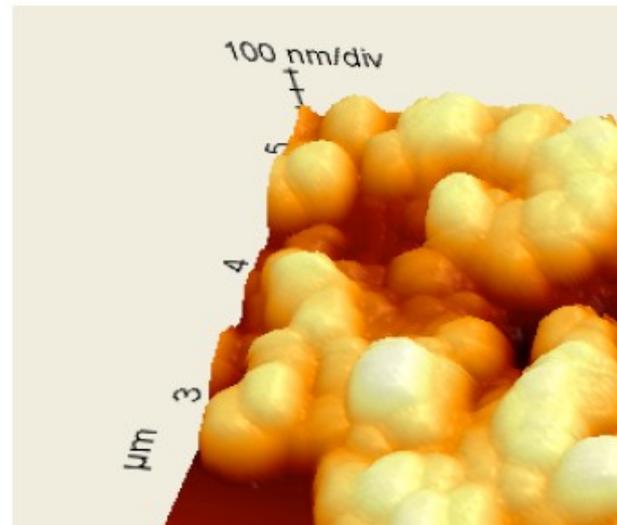


# AFM on Highly Oriented Pyrolytic Graphite



**3H<sub>2</sub> on 6H<sub>2</sub>**

*Sergent-soldier effect*



# Let me thank...



*Alessandro Porchetta*  
*Photocurrent Experiment*



*Floriana Di Giorgio*  
*Supported Phospholipids*



*Mario Caruso*  
*Fluorescence Experiments*



*Emanuela 'Tiger' Gatto*  
*The true boss of the Lab*



*Donato Monti*  
*Chiral porphyrins*