



Nanostrutture auto-organizzate:

entropia, monostrati e macchine molecolari

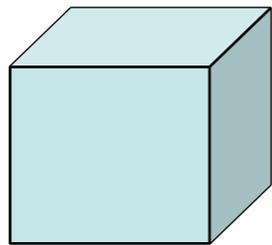
Valentina De Renzi

8 novembre 2011

Perche' nano?

perche' le proprieta' della materia a questa scala sono "speciali" e interessanti

materiali
3D



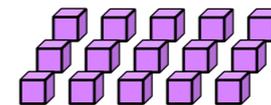
film
2D



nanofili
1D

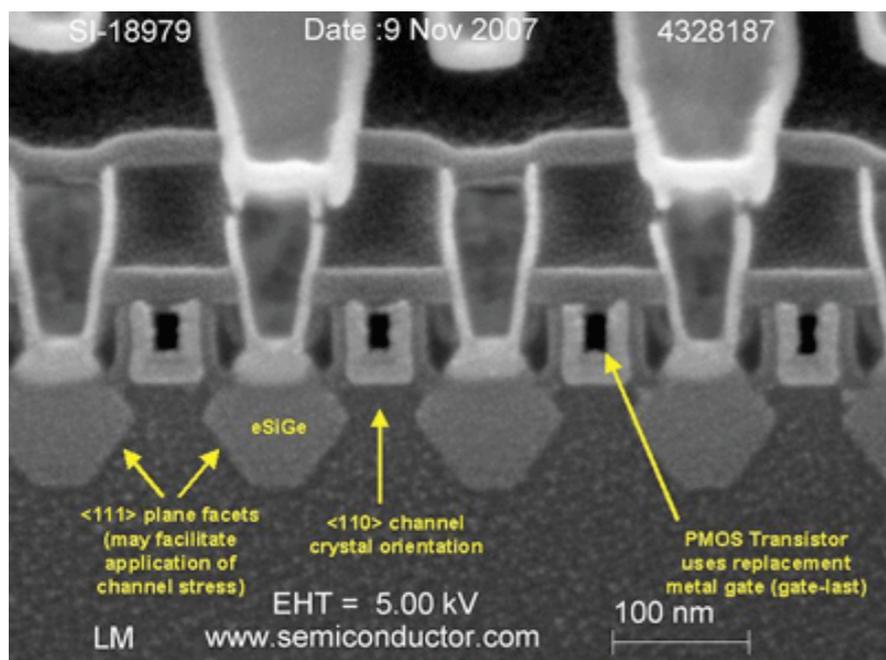


nanodots
0D

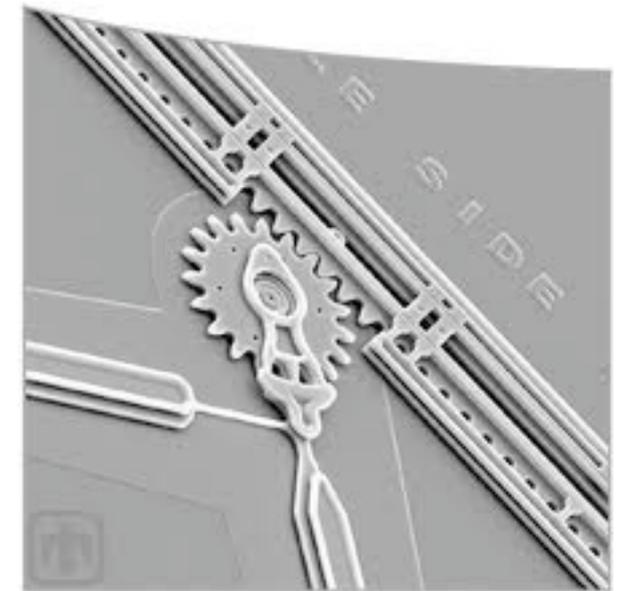
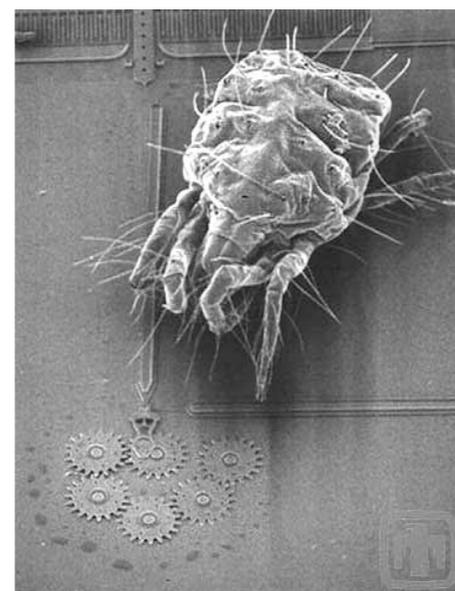


la tecnologia va verso il piccolo

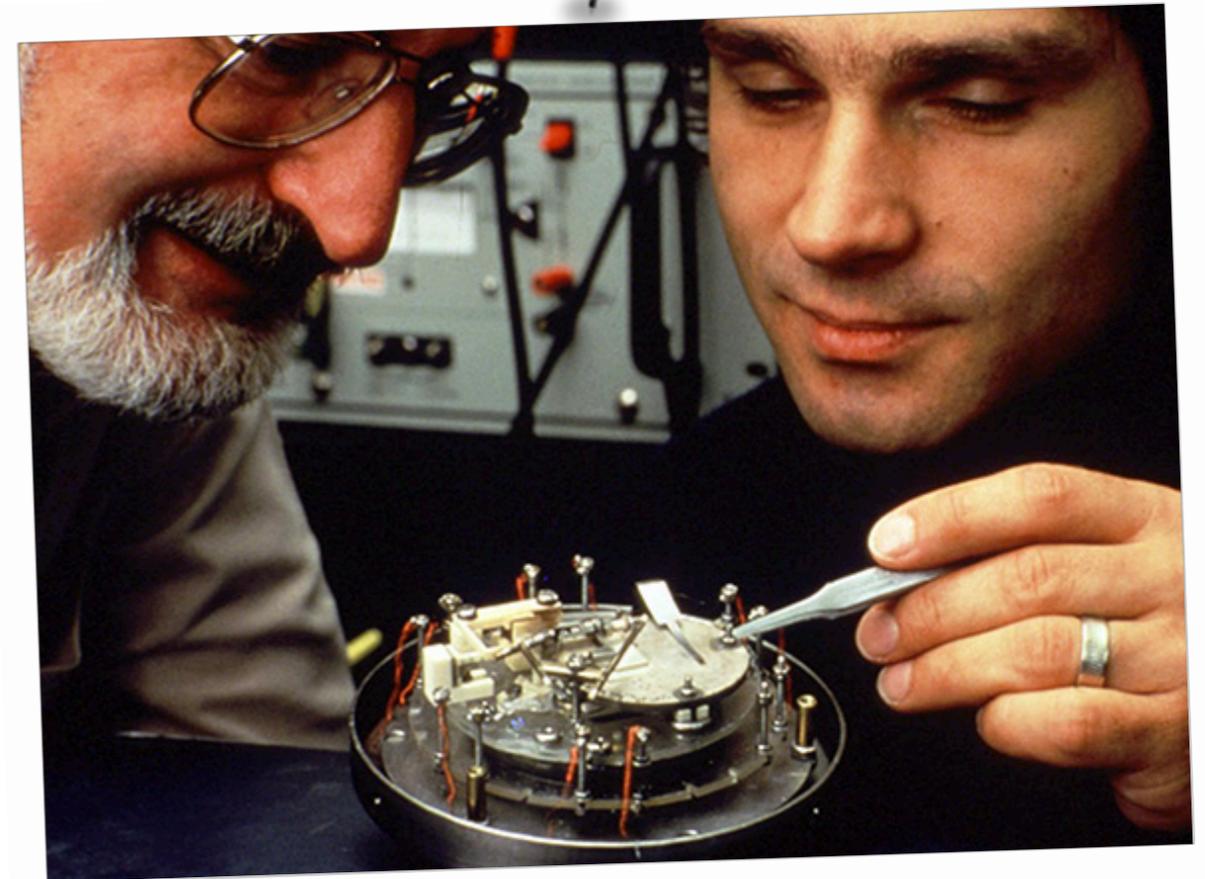
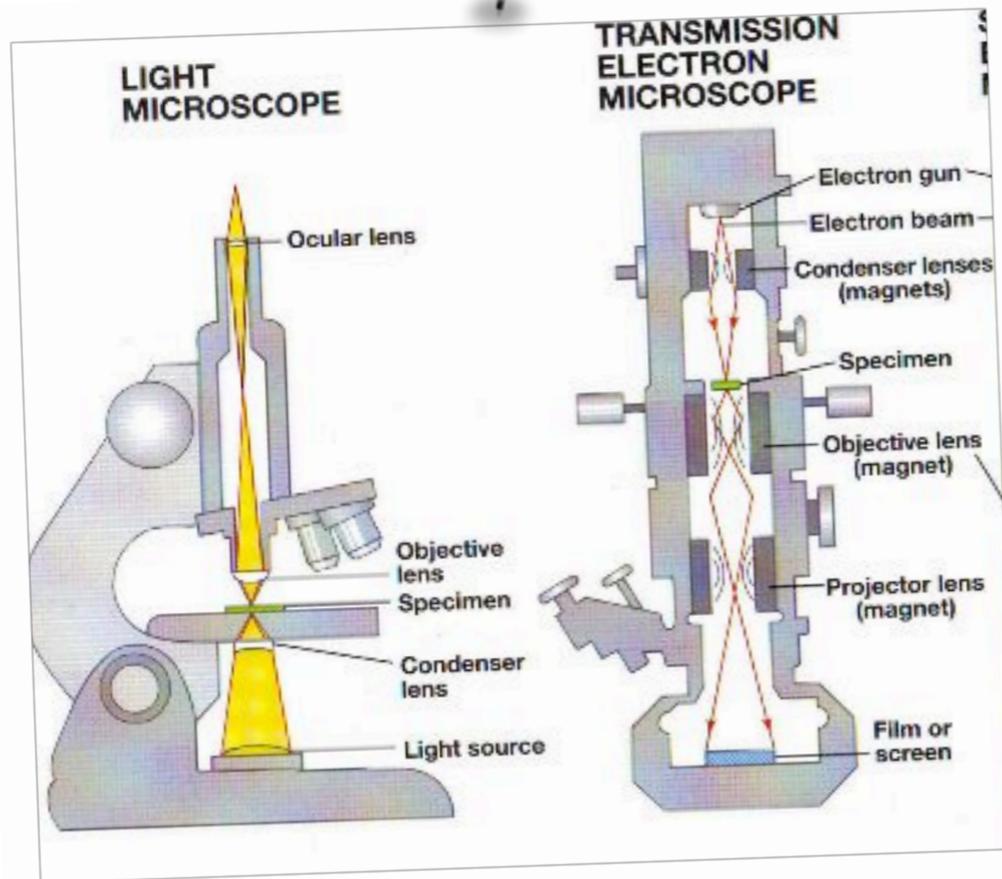
Transistor



Micro Electro-Mechanical Systems



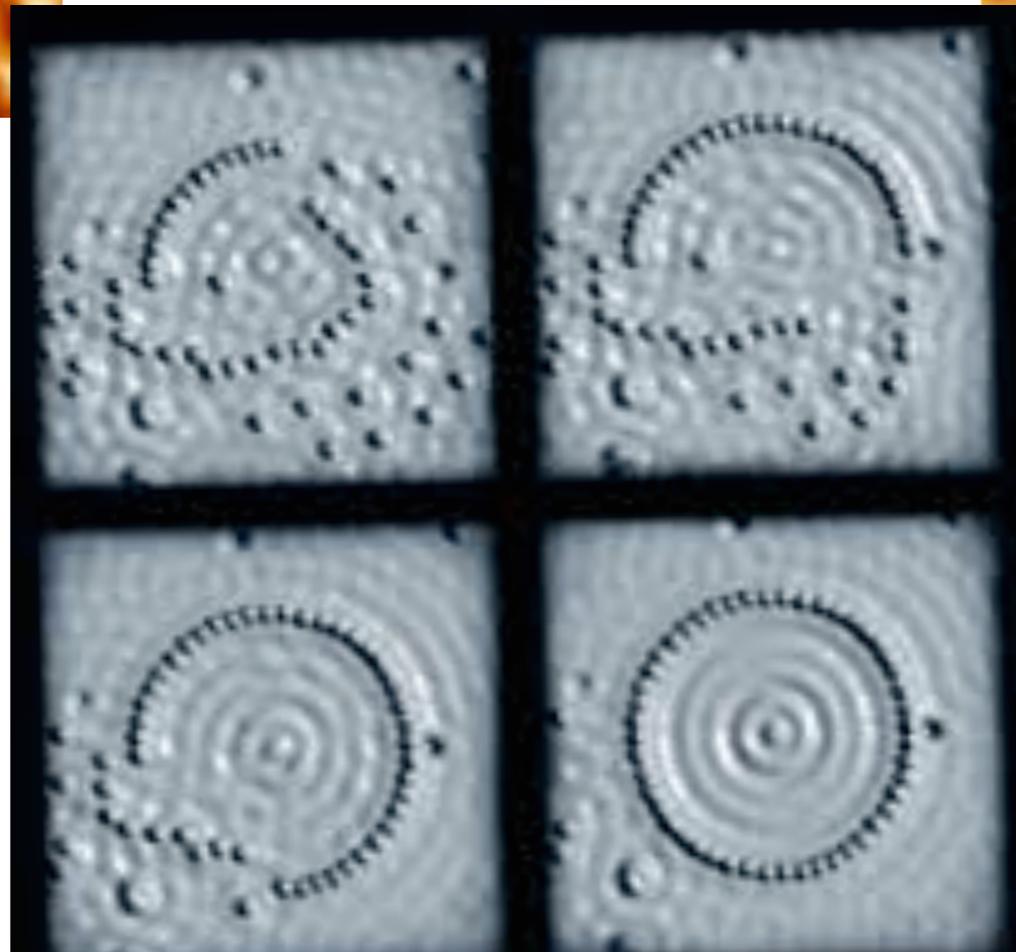
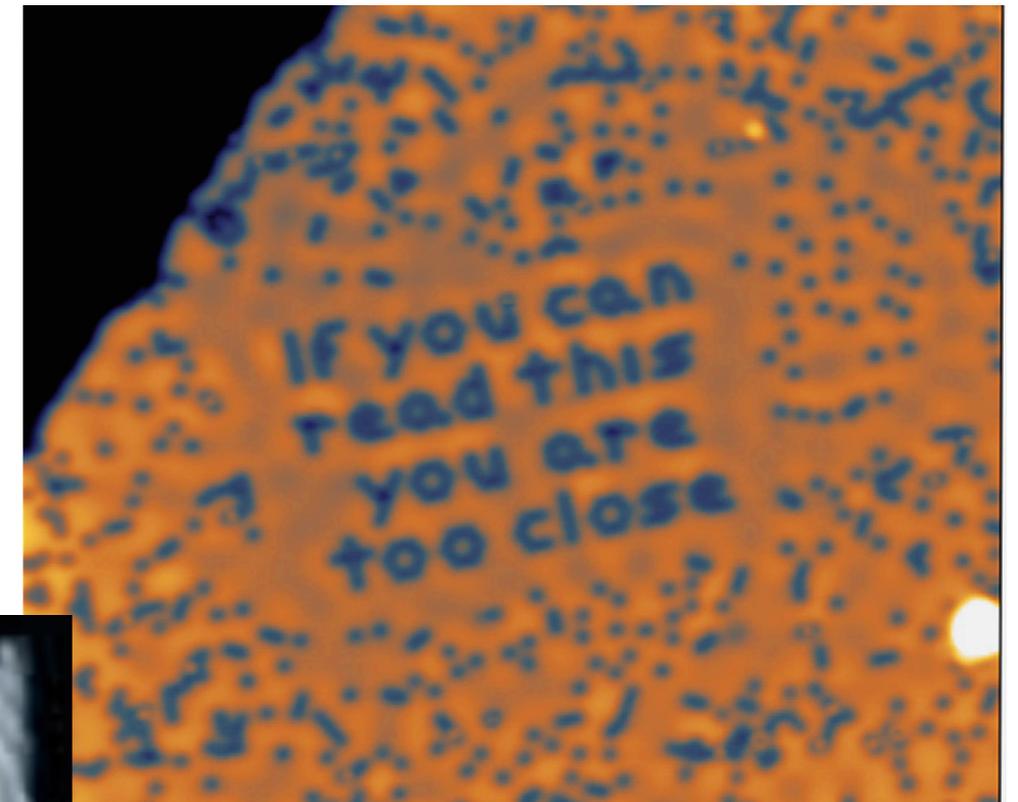
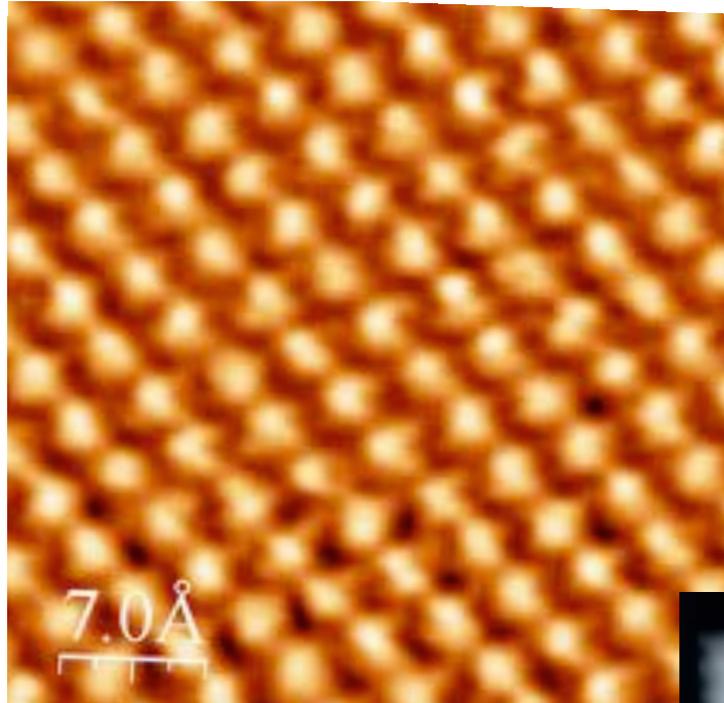
'Vedere' Nano: il microscopio elettronico e i microscopi a scansione



The Nobel Prize in Physics 1986
Ernst Ruska, Gerd Binnig, Heinrich Rohrer

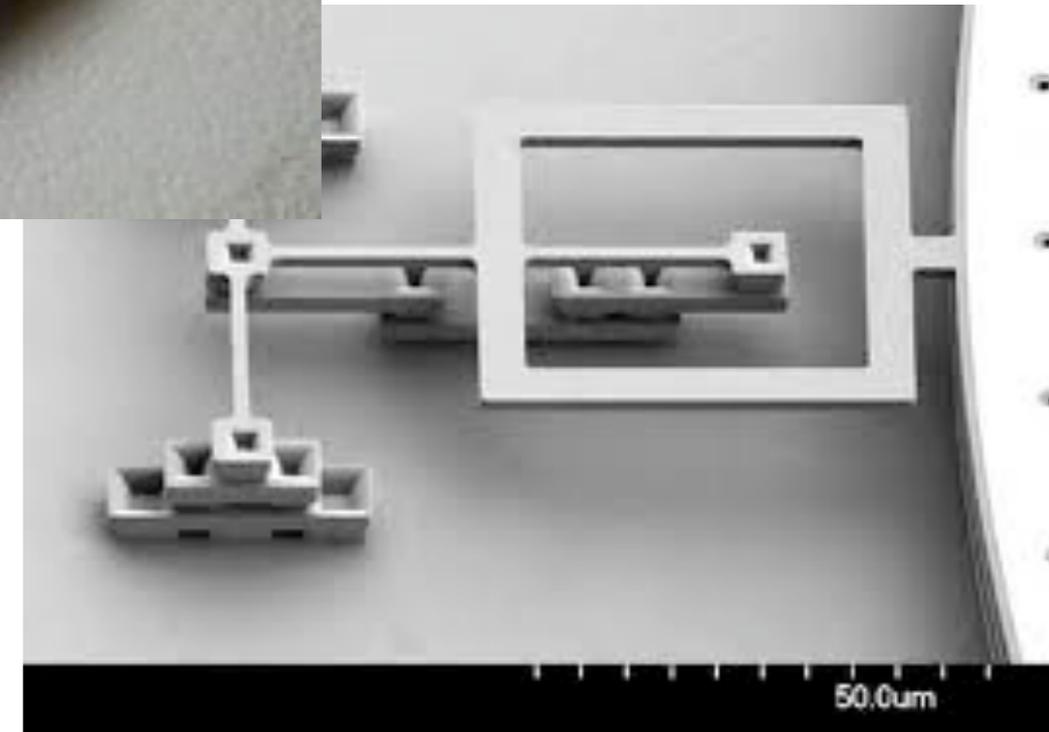
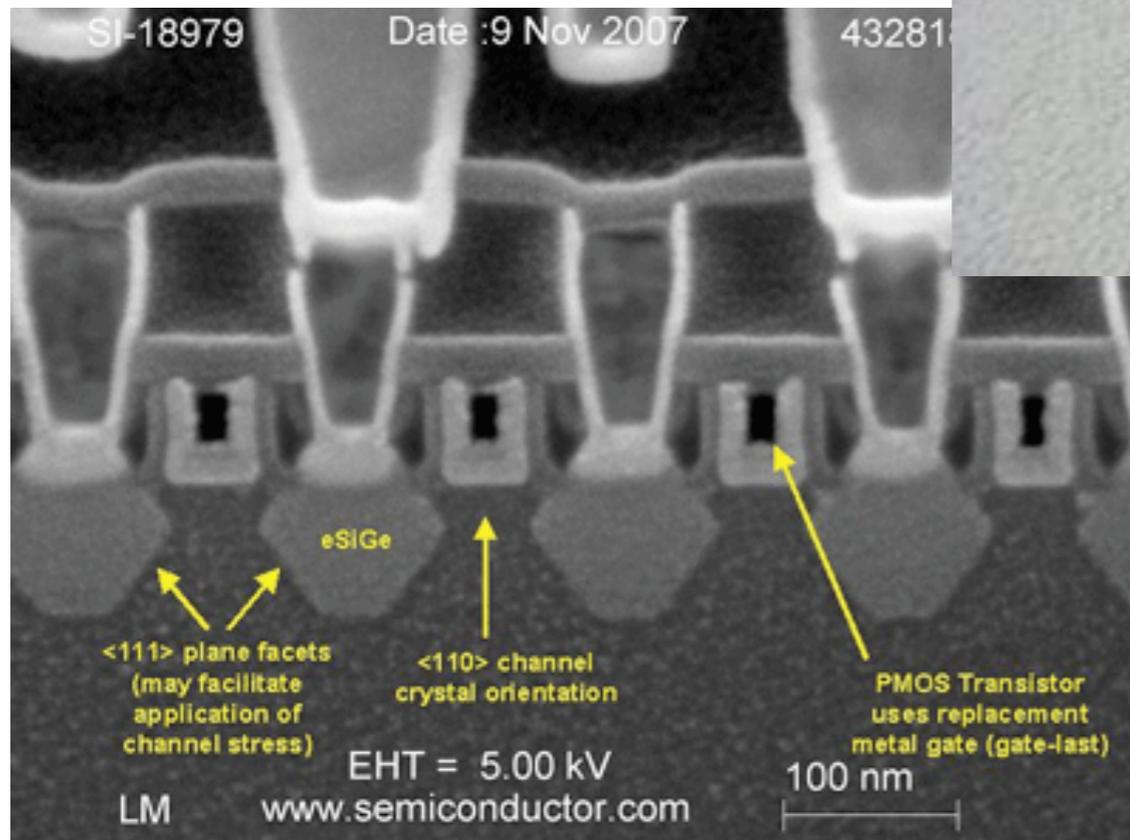
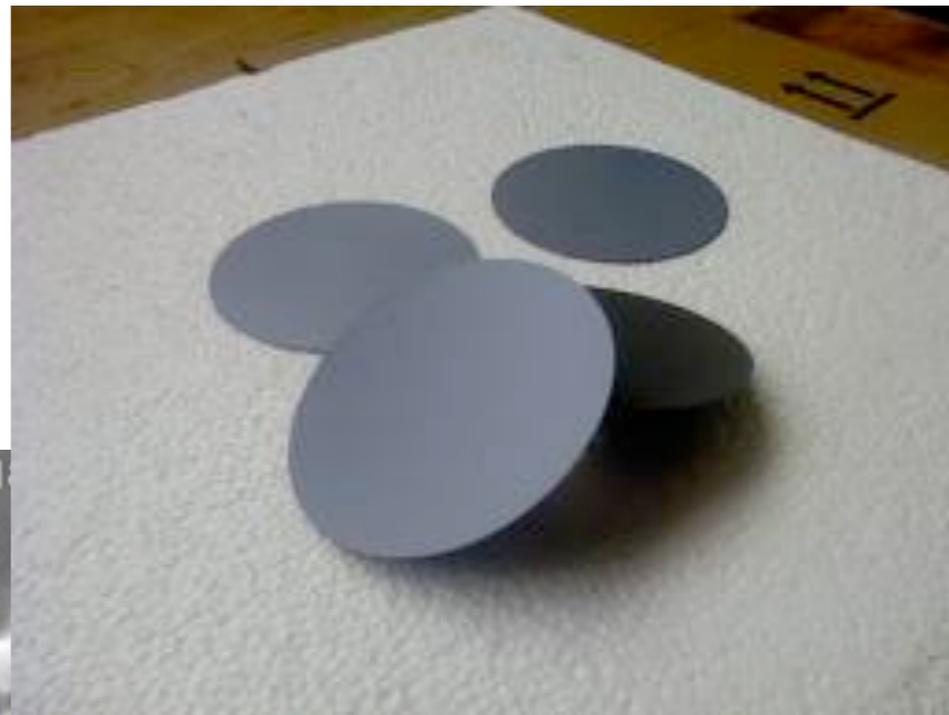
Lezione del 6 dicembre -
Stefano Frabboni e Guido Paolicelli

STM: vedere e manipolare gli atomi



Come si costruiscono nano-strutture?

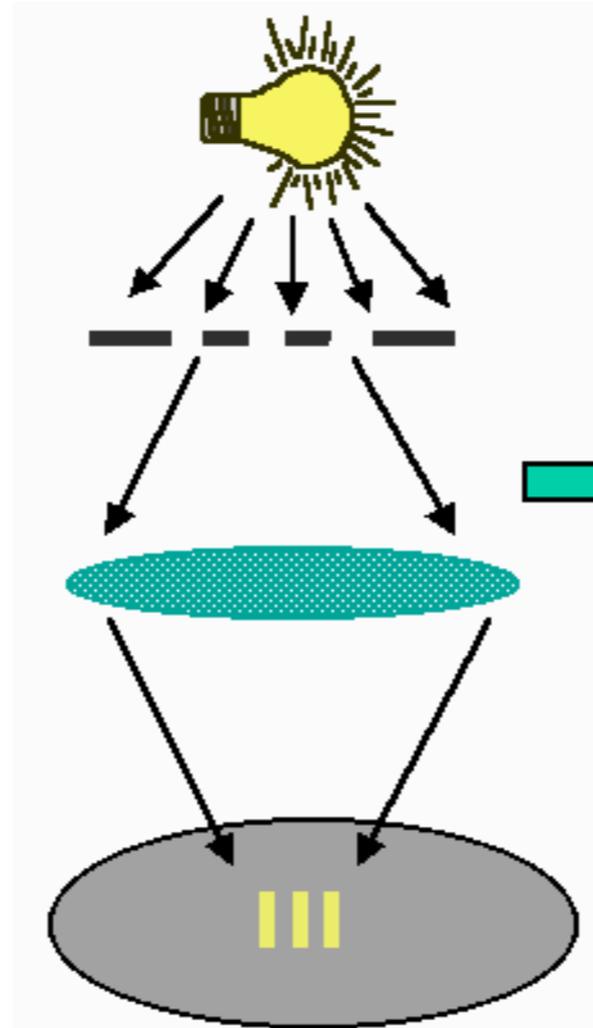
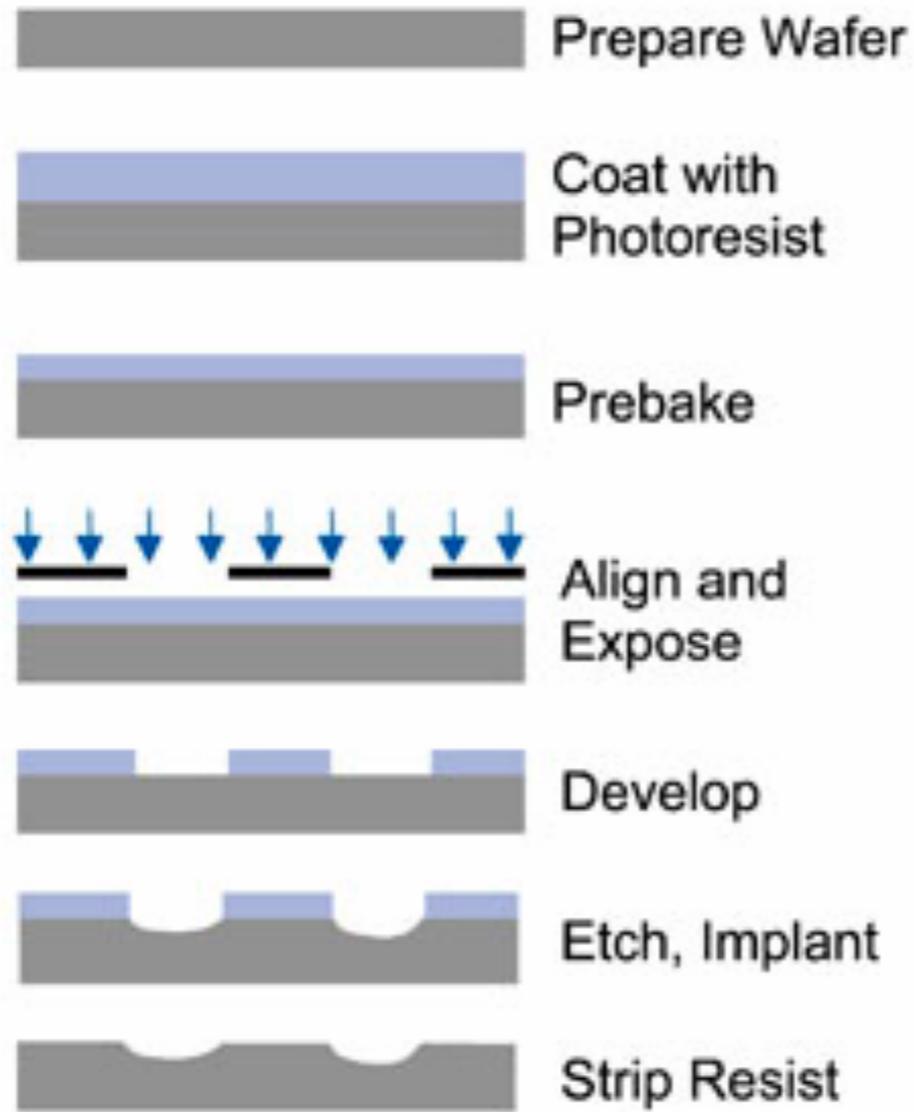
Fetta (wafer) di silicio cristallino



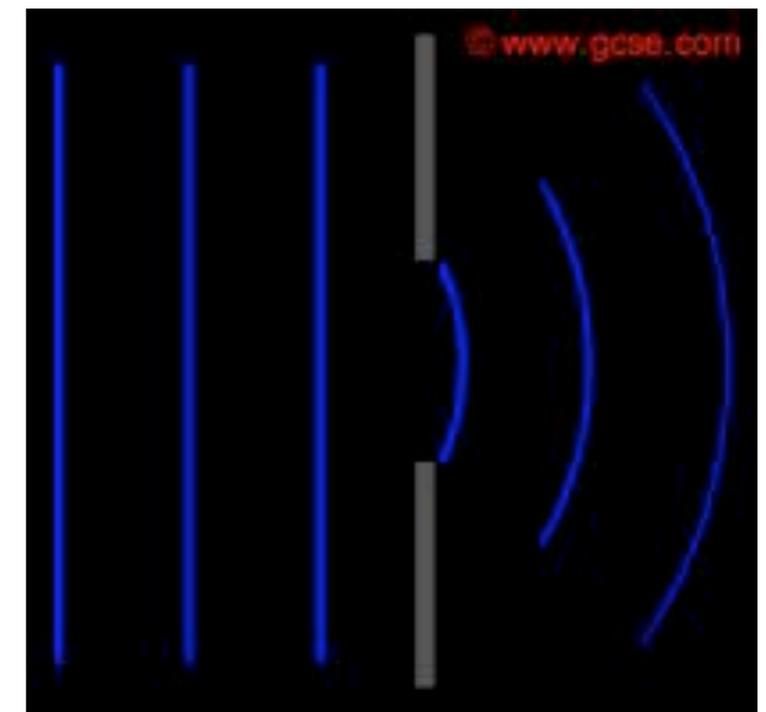
- Scavare
- Crescere ossido (isolante)
- Depositare metalli

Localmente!

La litografia (ottica)



Limite diffrattivo: non posso ne' "vedere" ne'
"disegnare" oggetti piu' piccoli della lunghezza
d'onda
UV ~ 100nm



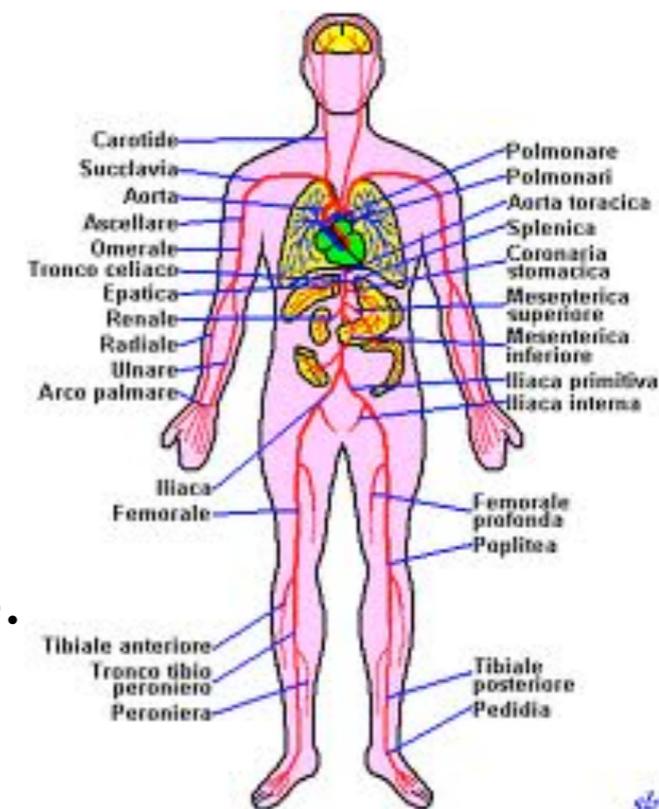
self-assembling

Formazione **spontanea** di una **struttura ordinata e complessa** a partire da componenti iniziali semplici

- Auto-organizzazione della materia vivente:
NOI, siamo auto-assemblati

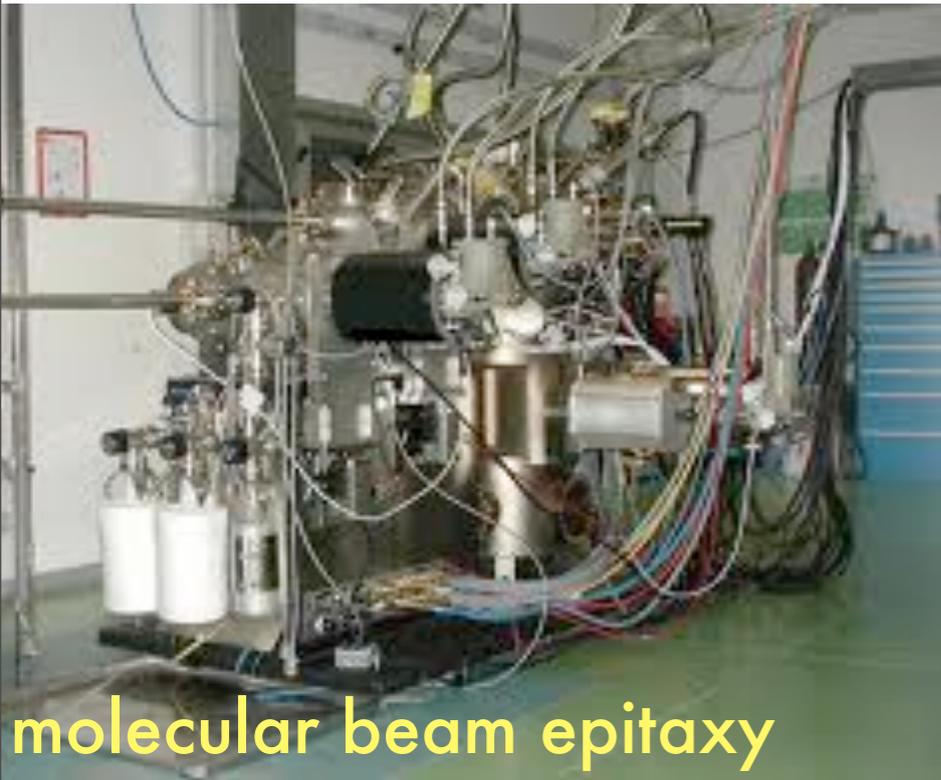


Formazione e distribuzione delle galassie nell'universo.

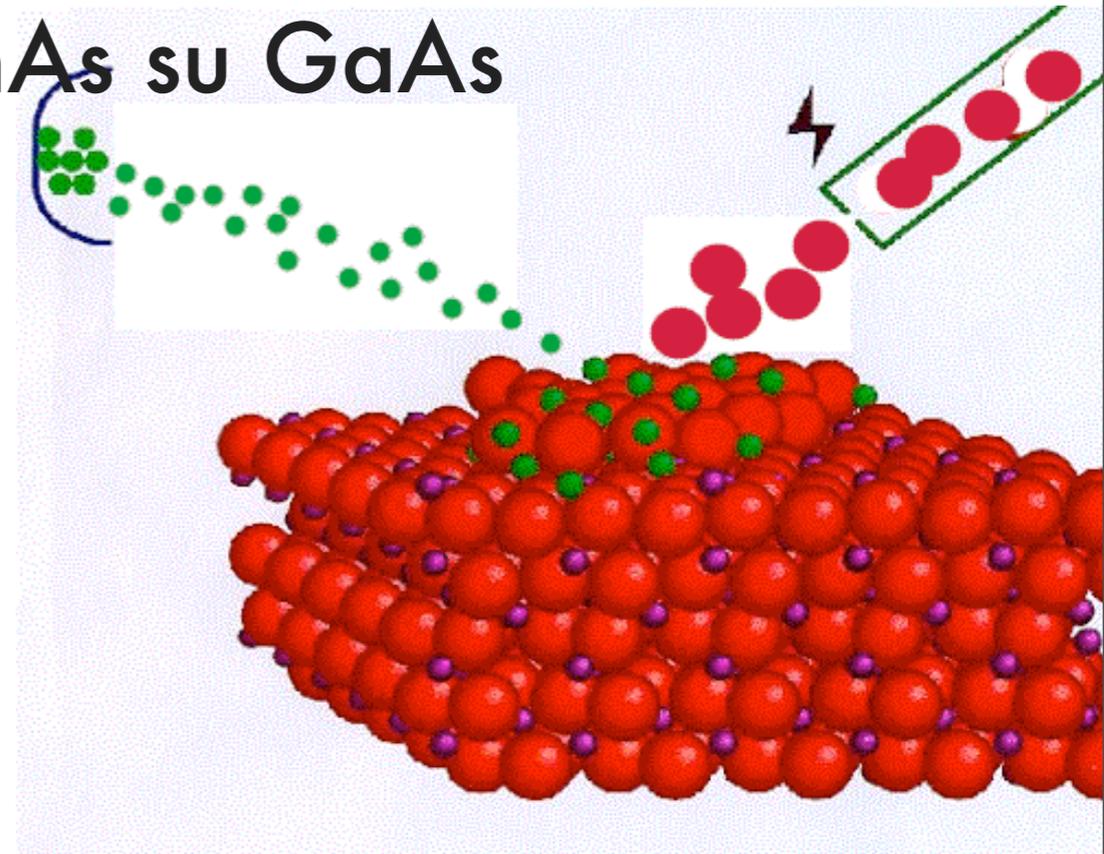


- Competizione fra interazioni diverse
- sistema con molti gradi di liberta

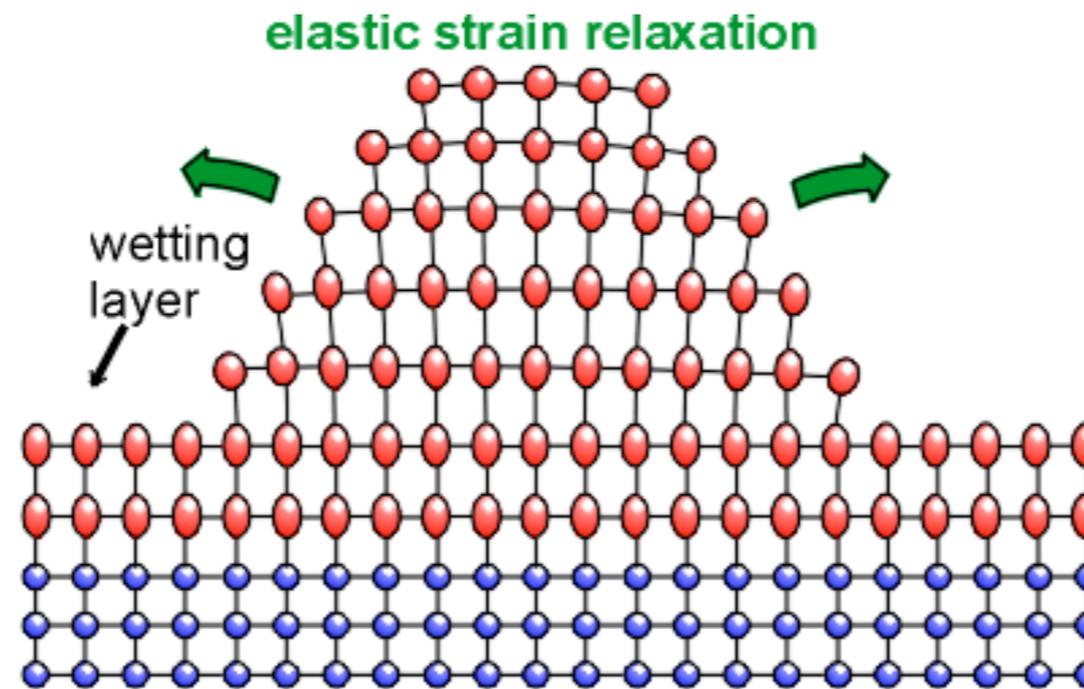
Crescita auto-organizzata di Quantum Dots



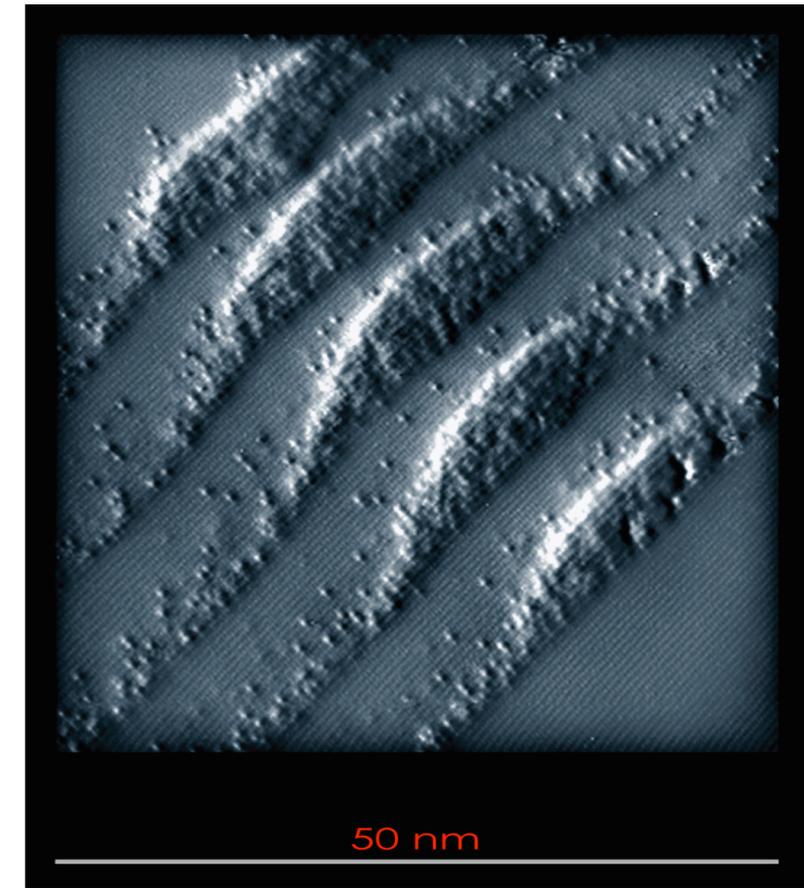
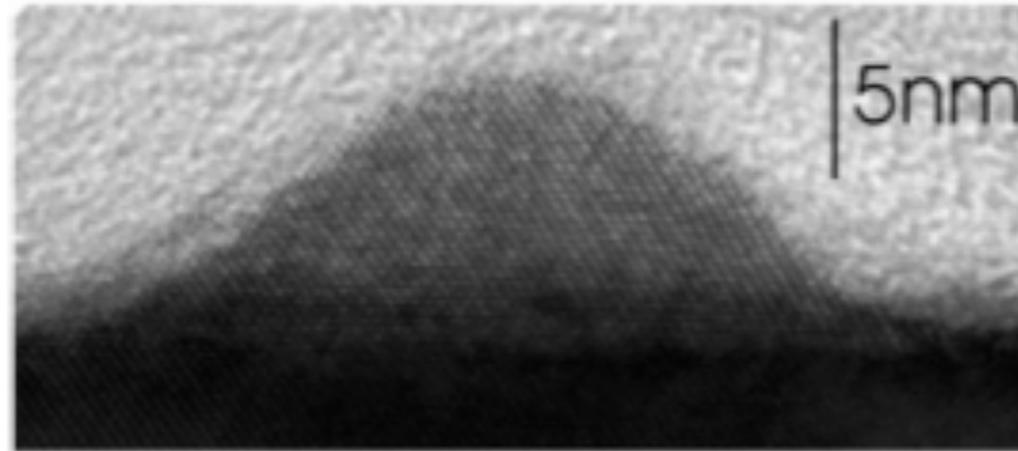
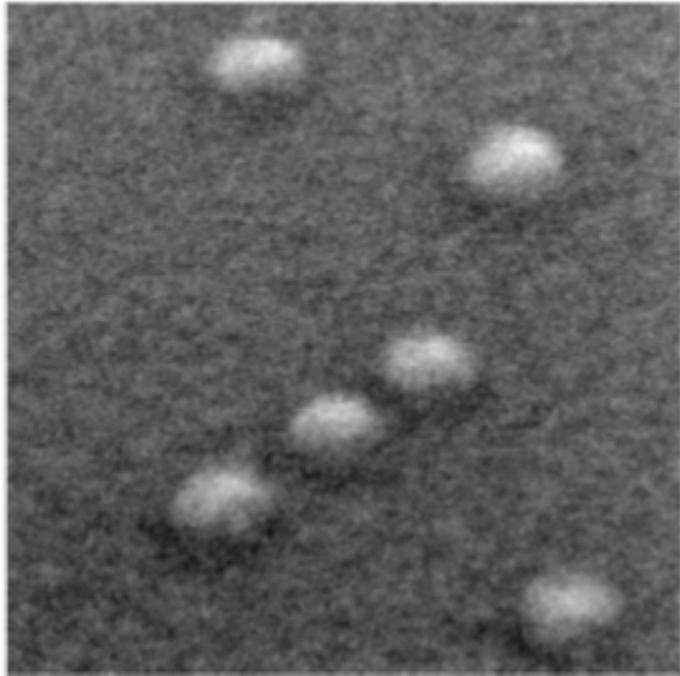
InAs su GaAs



La distanza fra atomi nel cristallo di InAs e' del 7% piu' grande rispetto al GaAs



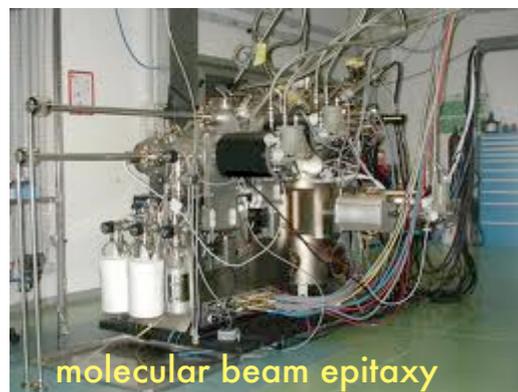
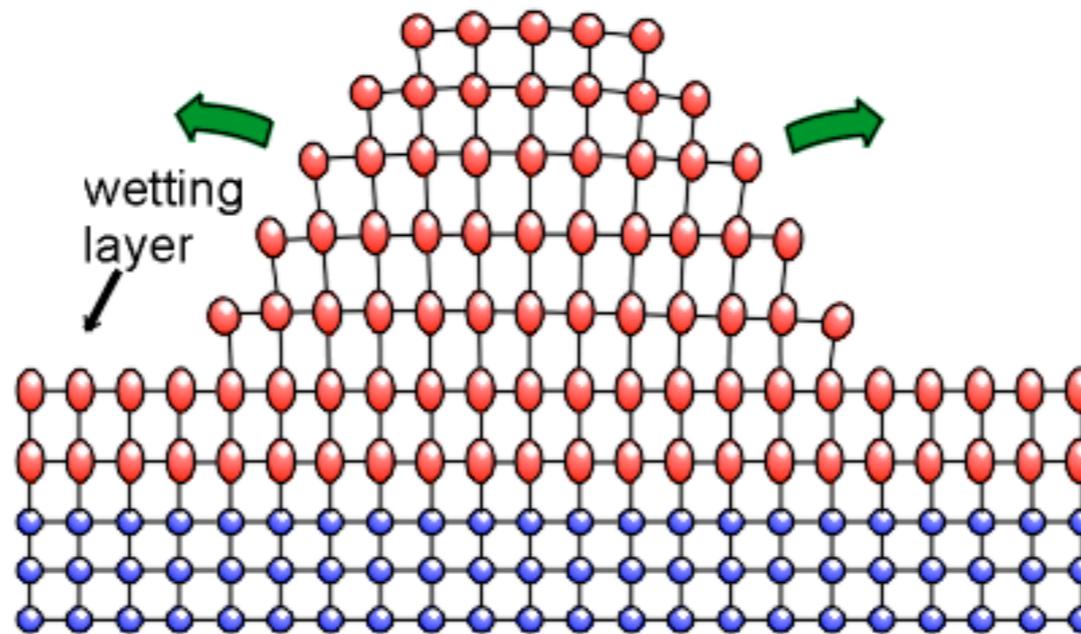
Crescita auto-organizzata di Quantum Dots



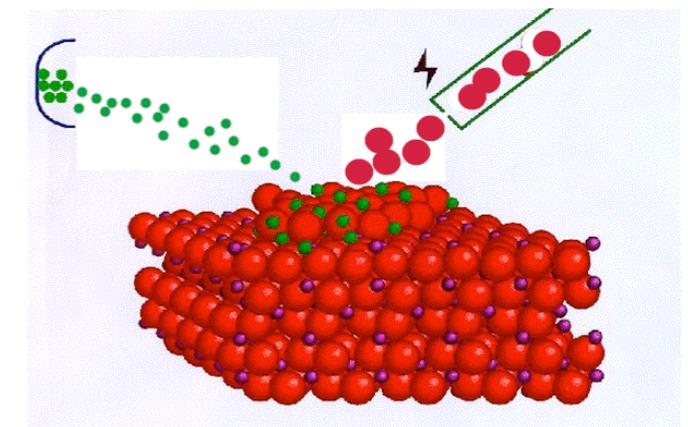
La distanza fra atomi nel cristallo di InAs e' del 7% piu' grande rispetto al GaAs

elastic strain relaxation

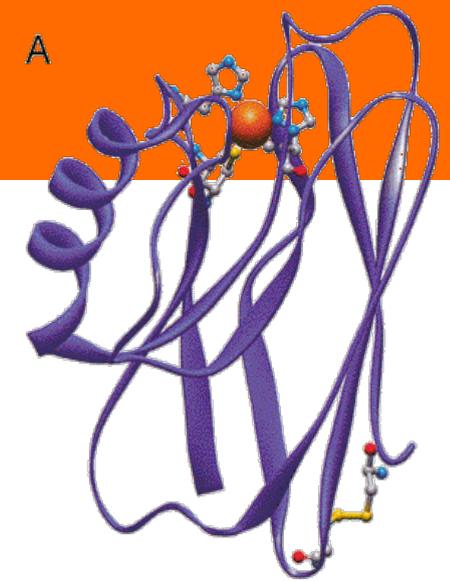
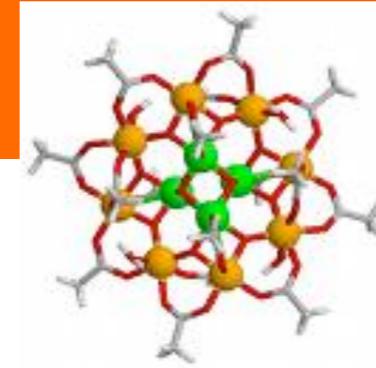
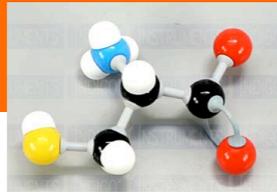
wetting layer



molecular beam epitaxy

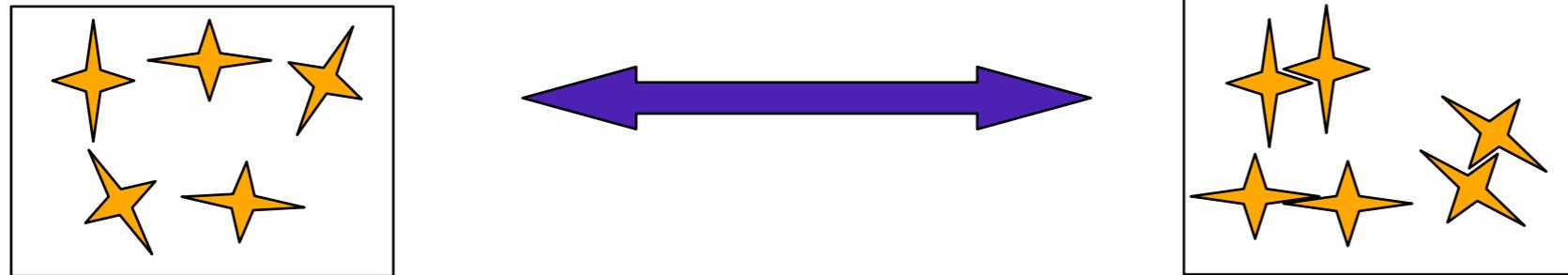


Self-assembling di le molecole organiche e biologiche



- Oggetti intrinsecamente 'nano' (1-10 nm) e identici
- Produzione (sintesi) e' un processo parallelo
- Posseggono molte funzioni e proprieta' (ottiche, elettroniche, meccaniche e magnetiche) interessanti modificabili per via chimica
- sono *intelligenti*: Si auto-organizzano formando strutture complesse e possono riconoscersi in modo selettivo
- materiali e metodi di nanostrutturazione potenzialmente piu' economici/ecologici

Self-assembling: processo **termodinamico** **spontaneo**



ΔU variazione di energia interna: energia di legame fra le molecole

ΔS variazione di entropia durante il processo

Primo principio $\Delta U = \Delta Q - \Delta W$

Secondo principio $\Delta Q \leq T \Delta S$

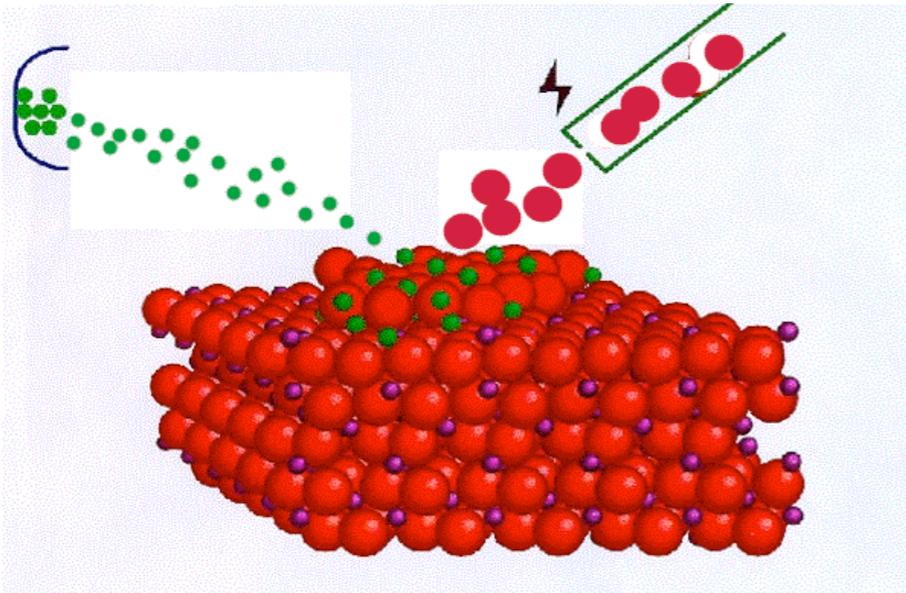
$$\Delta U \leq T \Delta S - \Delta W$$

T, V cost $\Delta(TS) = T \Delta S$ e $\Delta W = 0$ Energia libera di Helmotz $F = U - TS$

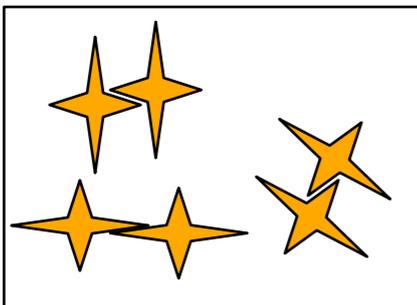
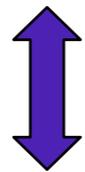
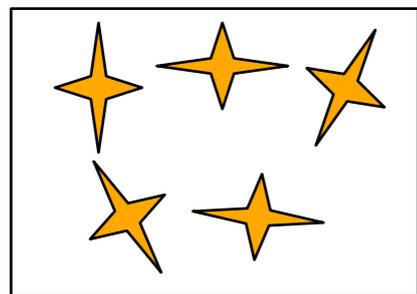
$$\Delta F = \Delta(U - TS) = \Delta U - T \Delta S \leq 0$$

il sistema tende spontaneamente allo stato che minimizza F

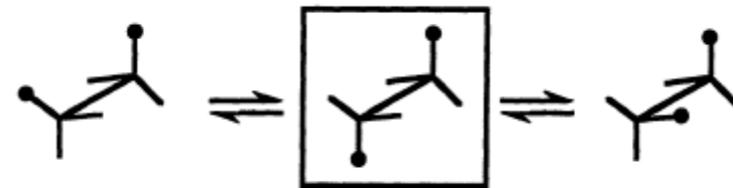
Processo spontaneo: $\Delta F = \Delta U - T\Delta S \leq 0$



Legami covalenti : ΔU domina (a basse temperature)

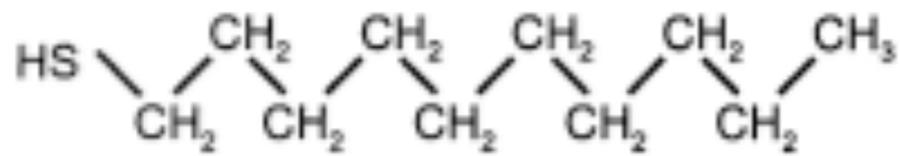
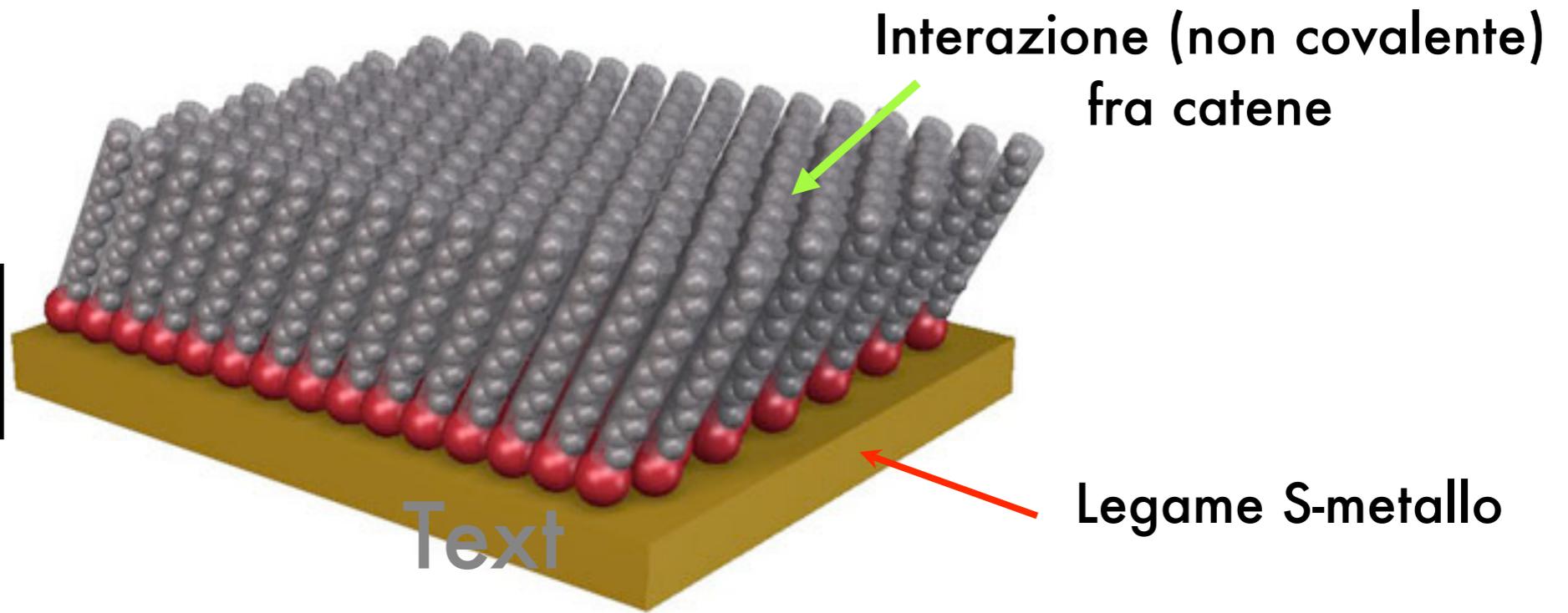
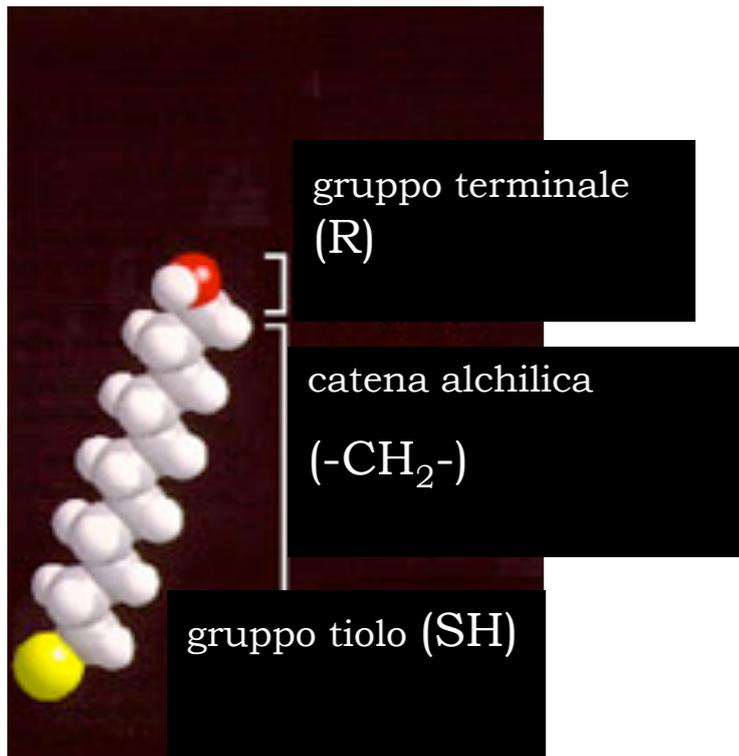


Interazioni non-covalenti:
il fattore entropico e' determinante



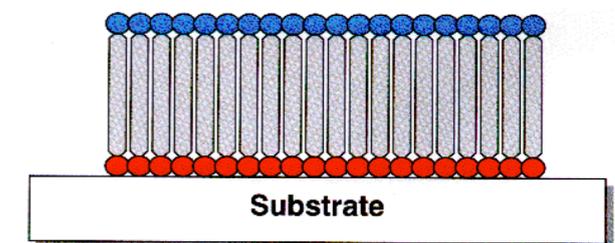
piu' il numero di gradi di liberta` che vengono congelati dall'aggregazione e` alto
piu' il contributo entropico diventa rilevante

Esempio: Self Assembled Monolayer

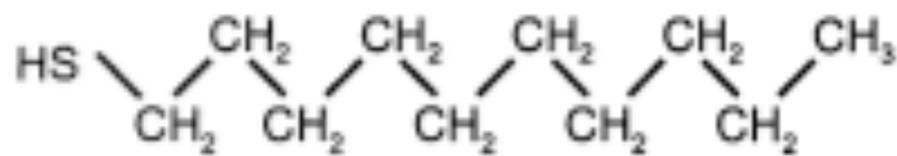
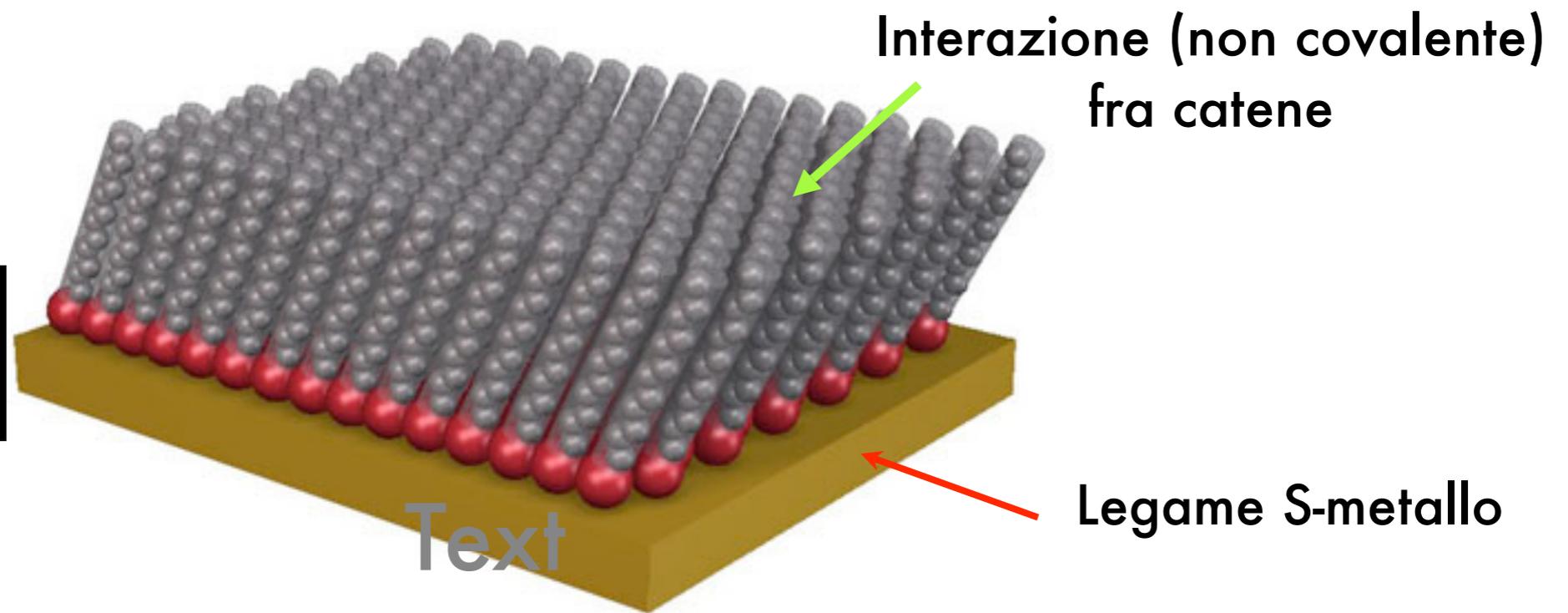
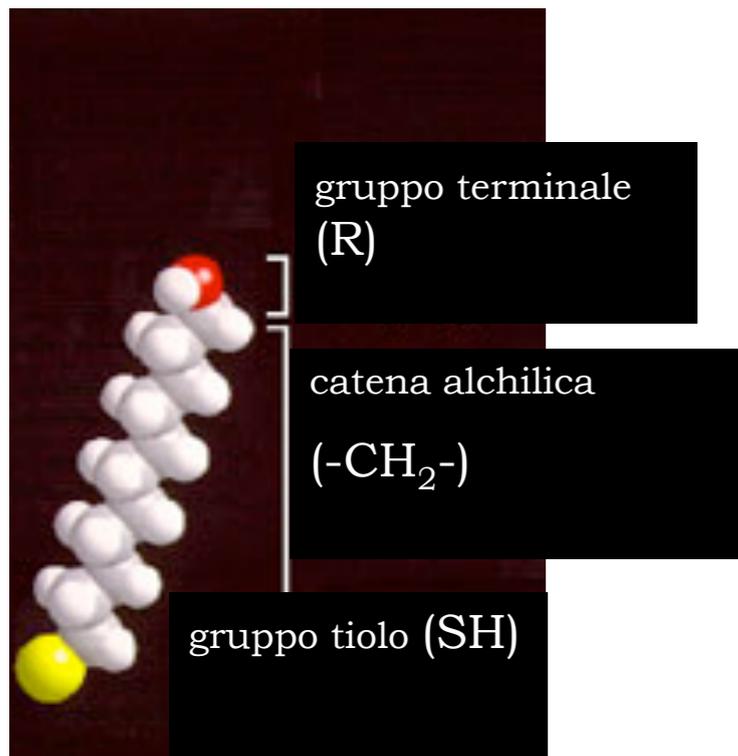


Metallo: Oro, Ag, Cu Pt; (111), (110), (100)

Formazione **monostrato SI** perche' $\Delta U(\text{molecola-substrato}) > T\Delta S$



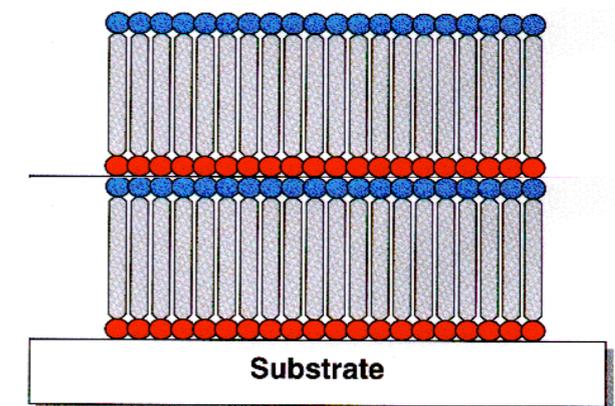
Esempio: Self Assembled Monolayer



Metallo: Oro, Ag, Cu Pt; (111), (110), (100)

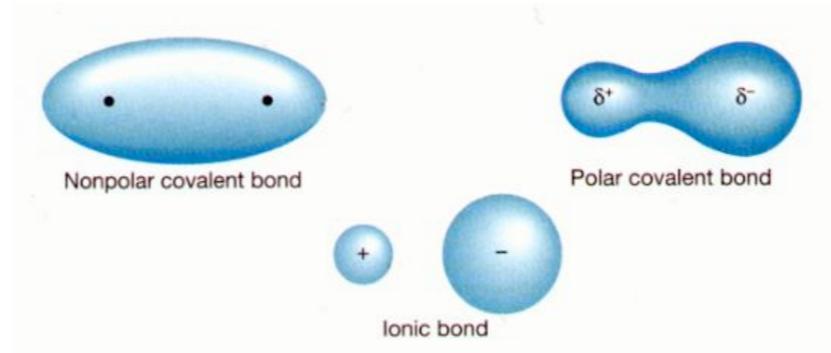
Formazione **multistrato**: **NO** perche' $\Delta U(\text{molecola-molecola}) < T\Delta S$

Formazione **monostrato** **SI** perche' $\Delta U(\text{molecola-substrato}) > T\Delta S$



Interazioni fra molecole

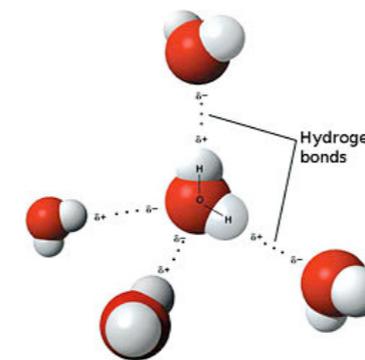
legame covalente



~ 1 eV

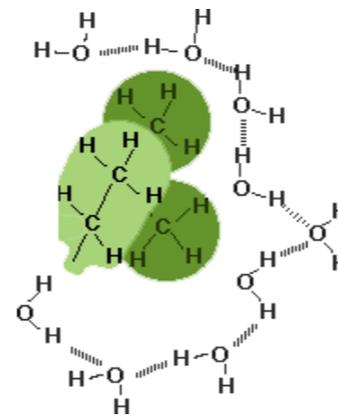
legame ionico

legami Idrogeno



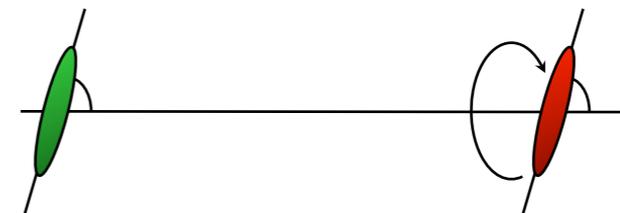
100-400 meV

Interazione idrofobica/ idrofilica



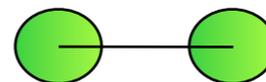
~ 200 meV

Interazioni fra dipoli



~ 25 meV

Van der Waals

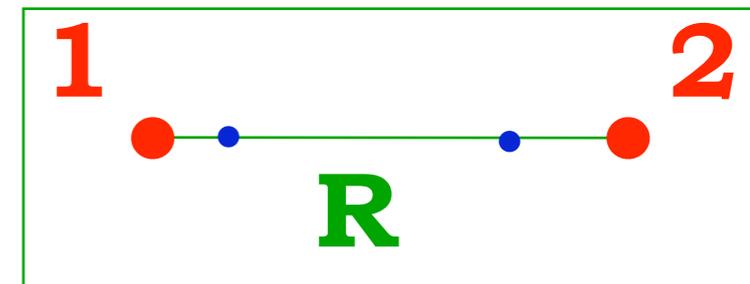
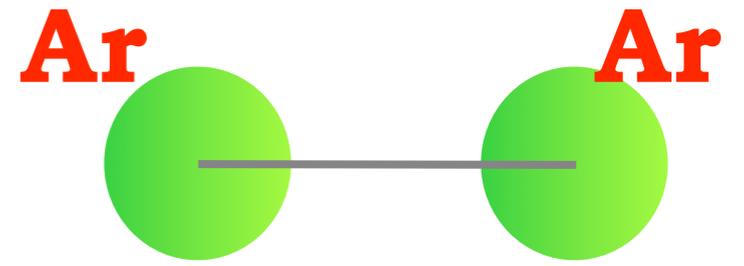
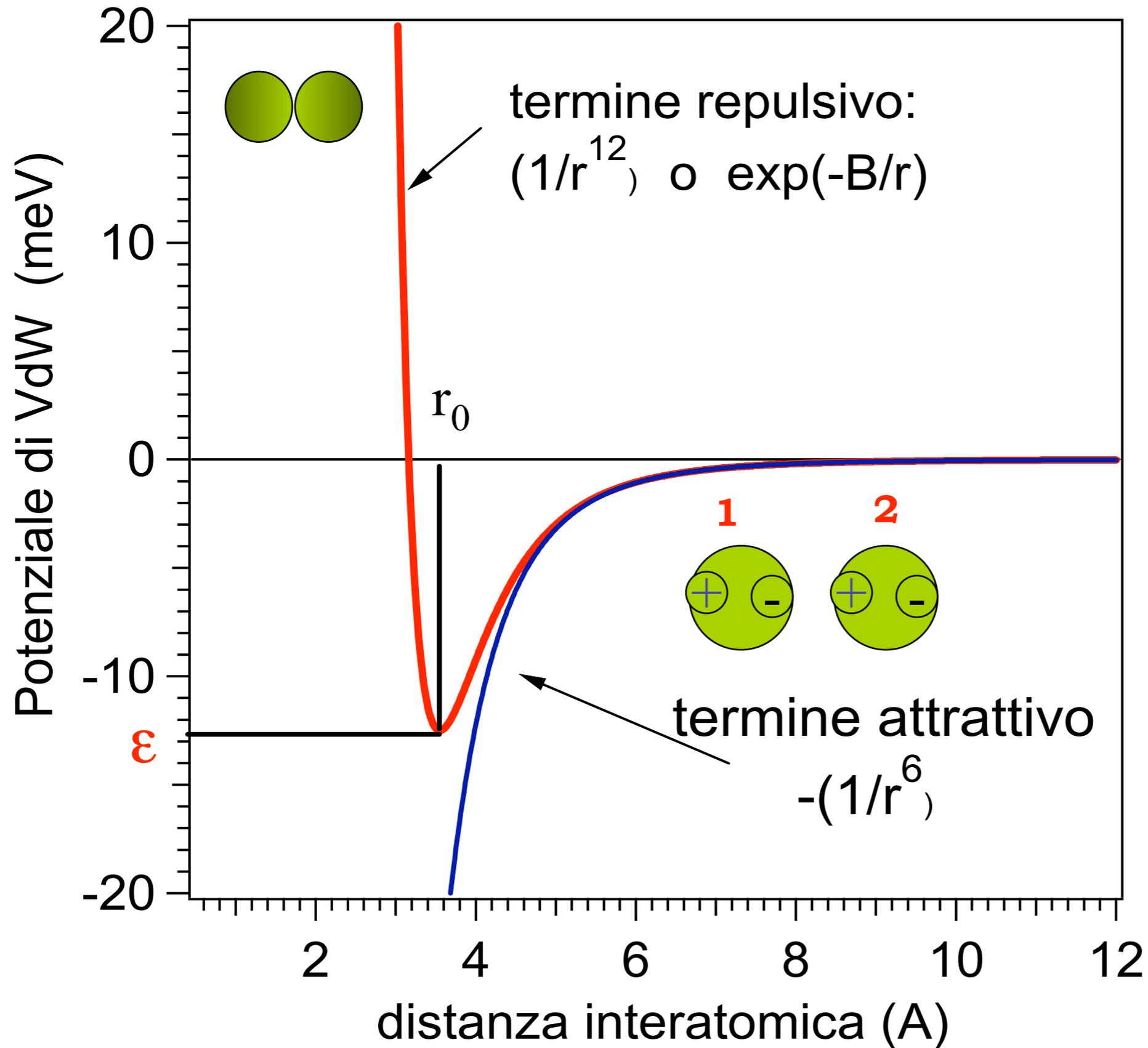


~ 10 meV/atomo

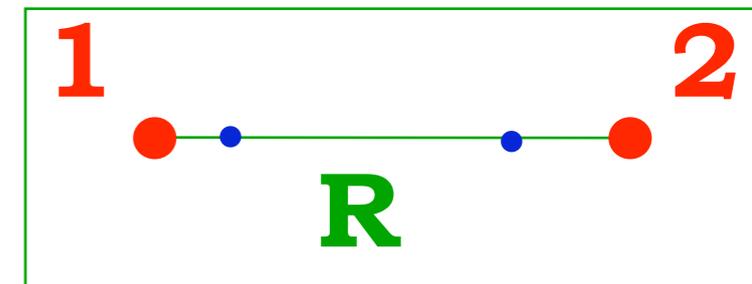
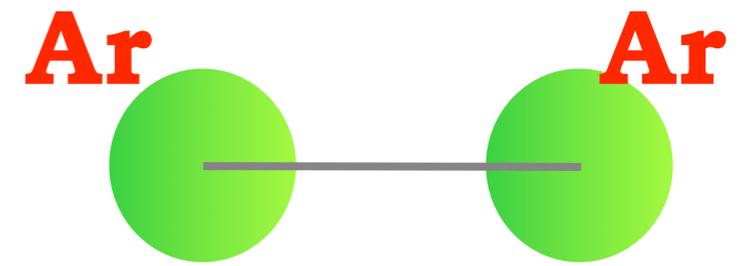
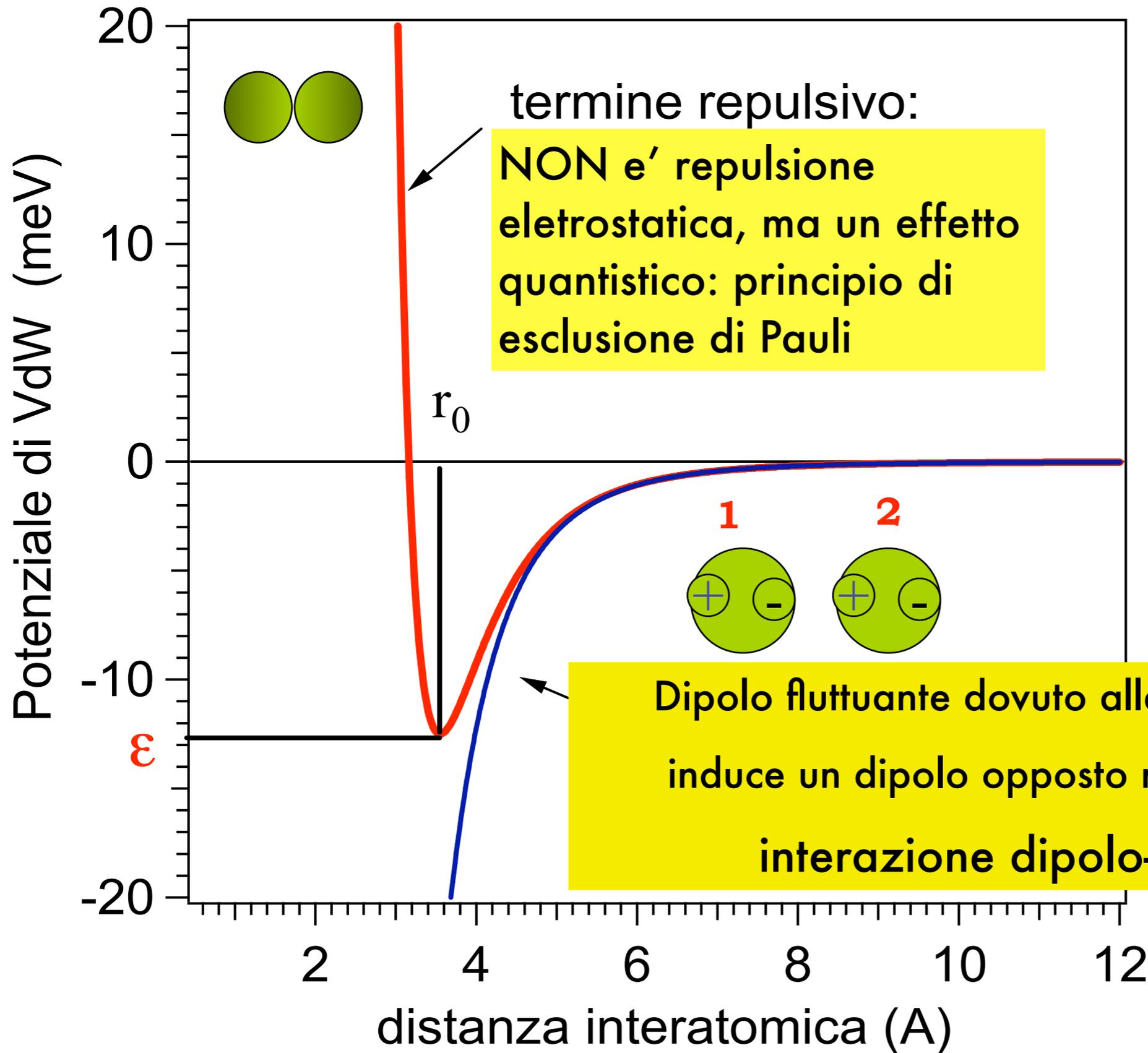
1 kcal/mole = 4.186 kJ/mole = 43 meV/molecola

KT=25 meV=0.6 kcal/mole

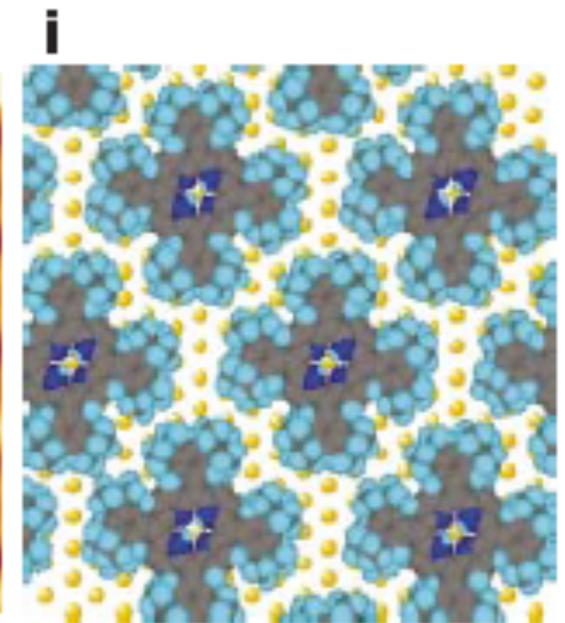
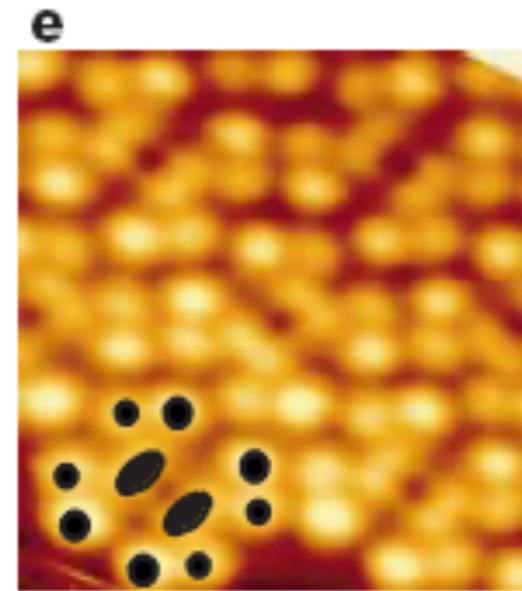
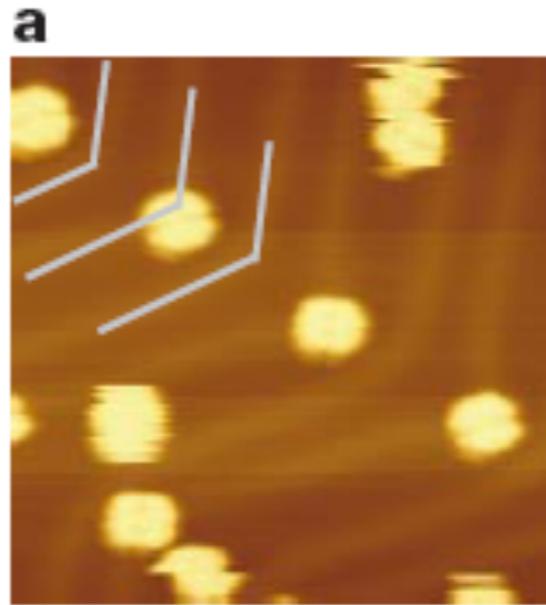
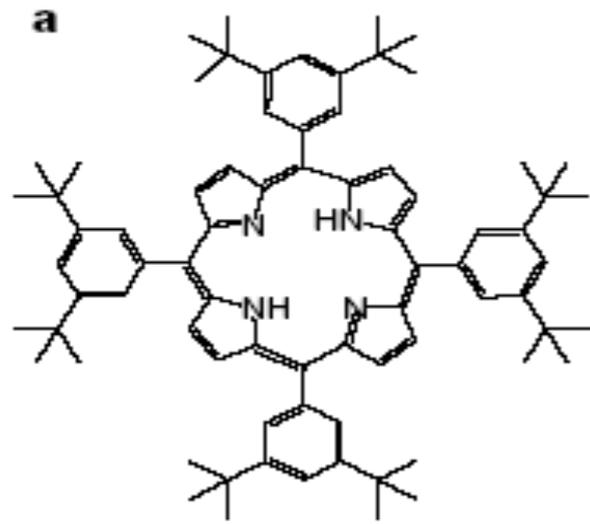
Forze di Van der Waals



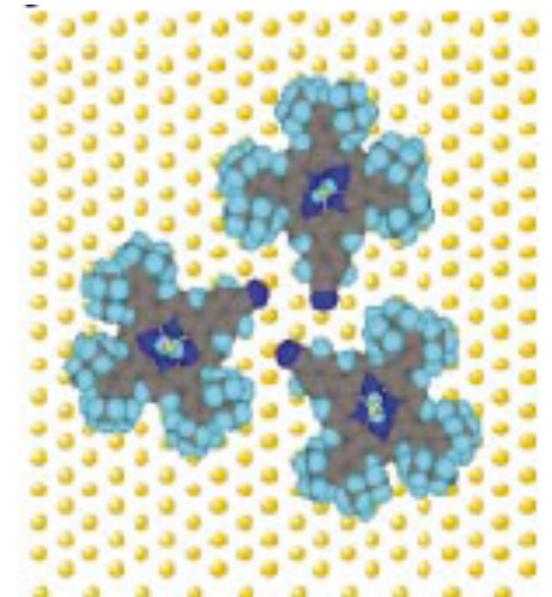
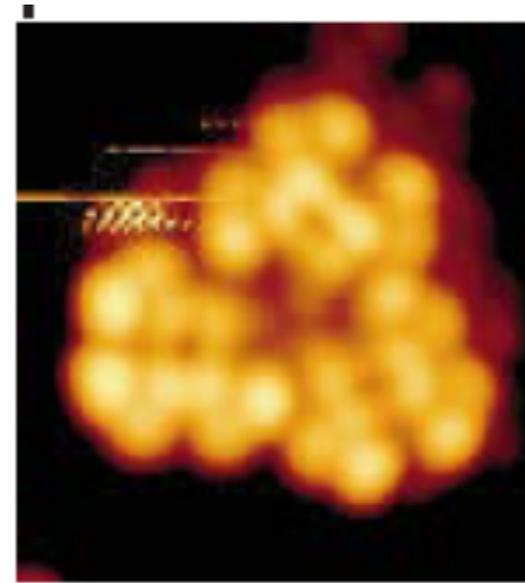
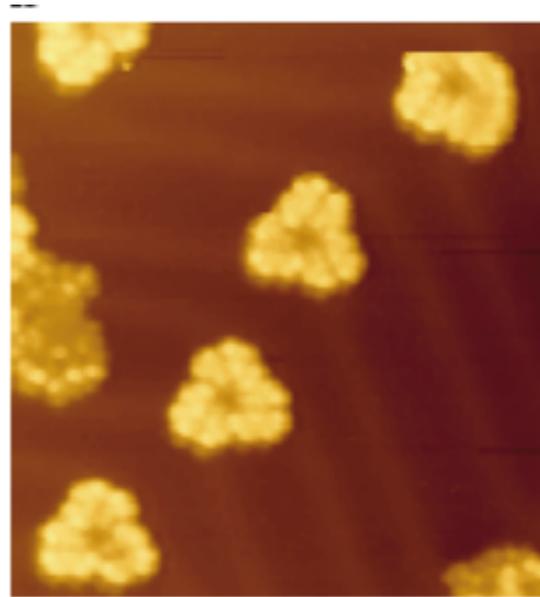
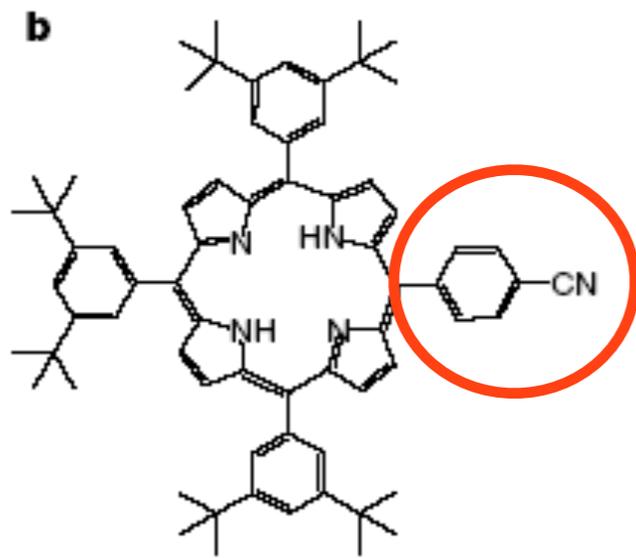
Forze di Van der Waals



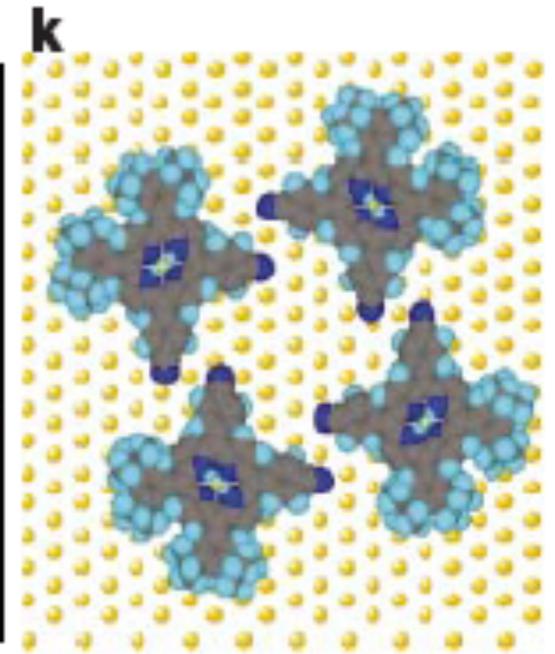
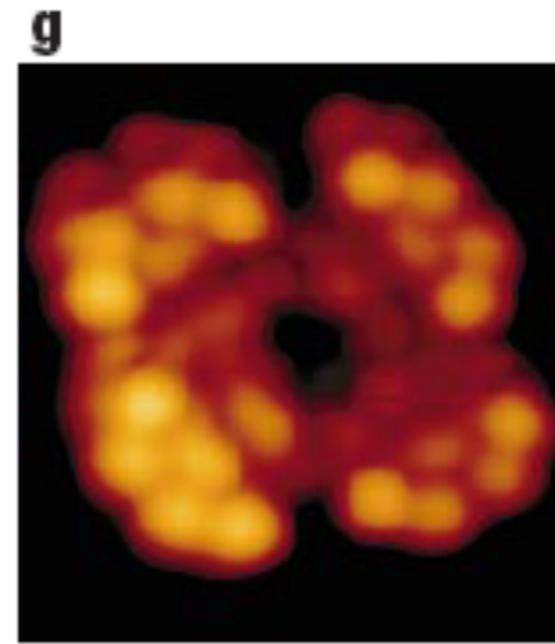
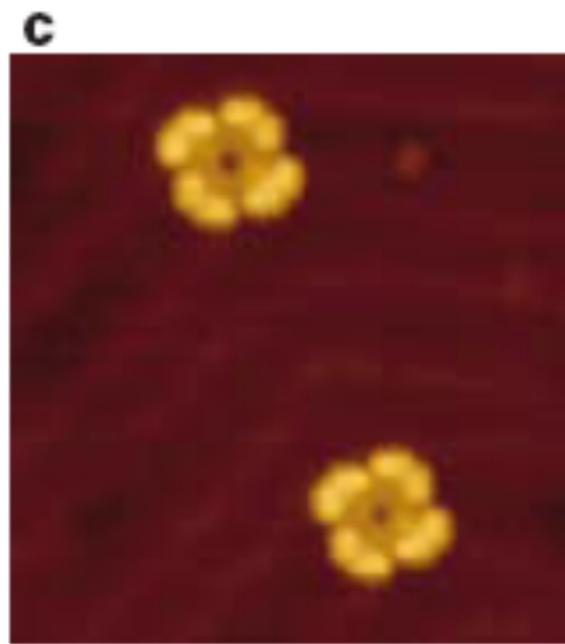
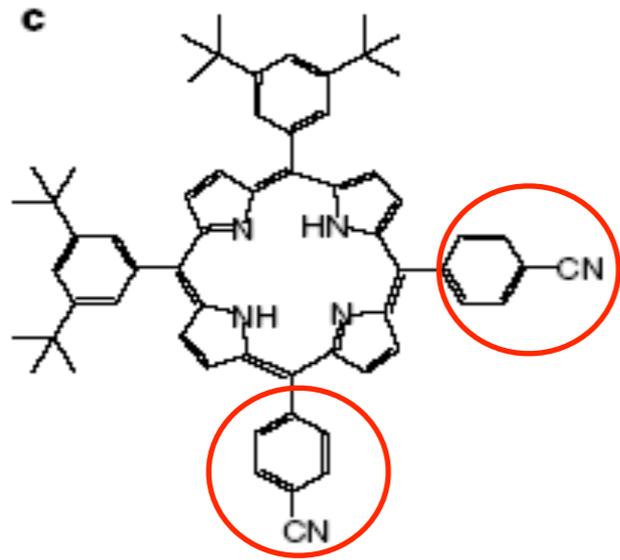
Auto-organizzazione di molecole organiche su superfici



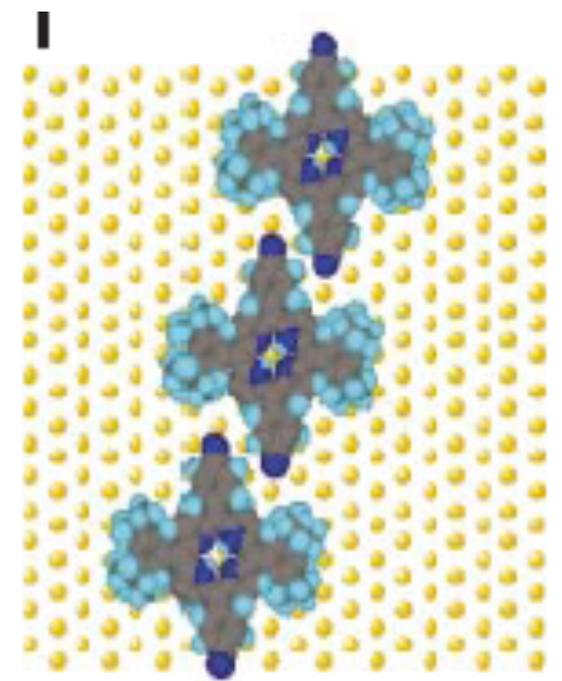
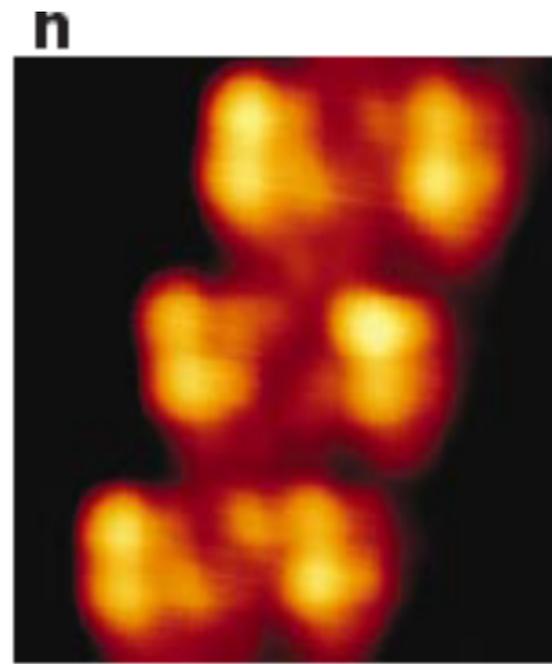
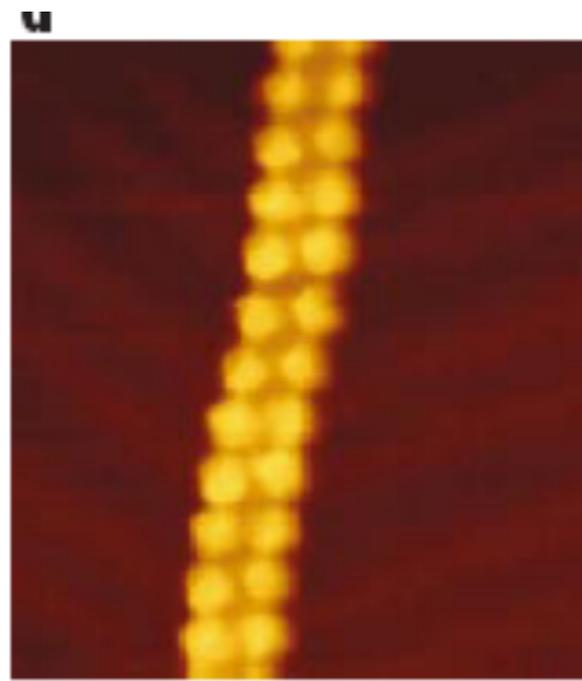
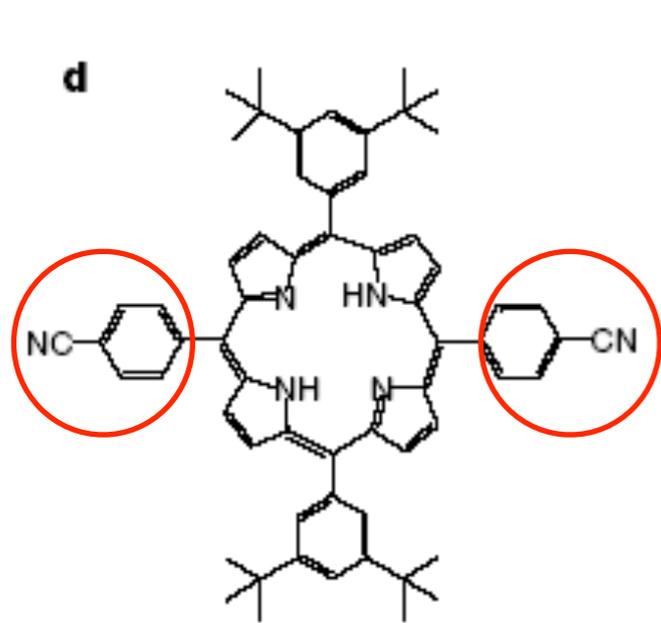
Auto-organizzazione di molecole organiche su superfici



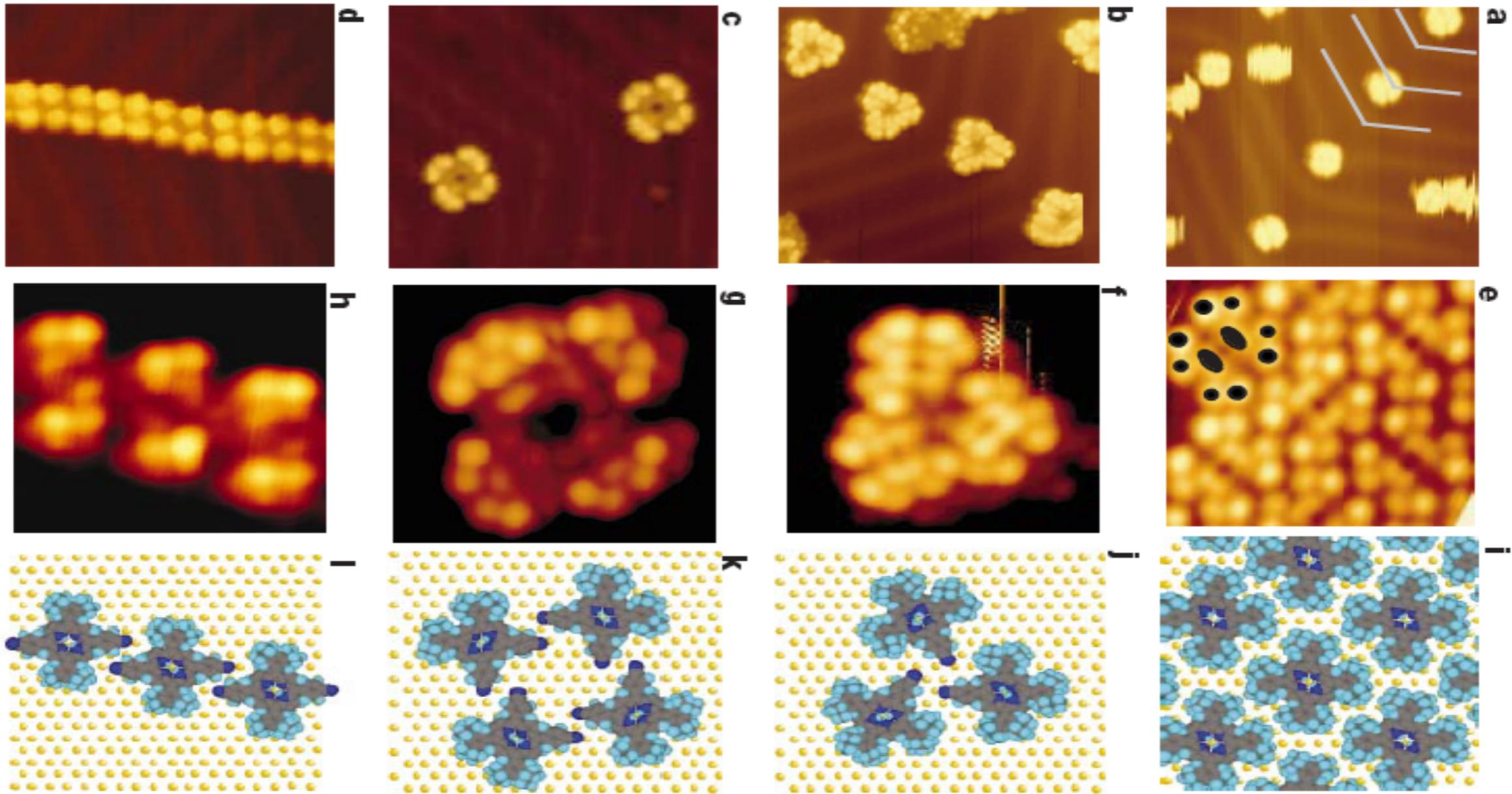
Auto-organizzazione di molecole organiche su superfici



Auto-organizzazione di molecole organiche su superfici



Auto-organizzazione di molecole organiche su superfici



Legame idrogeno

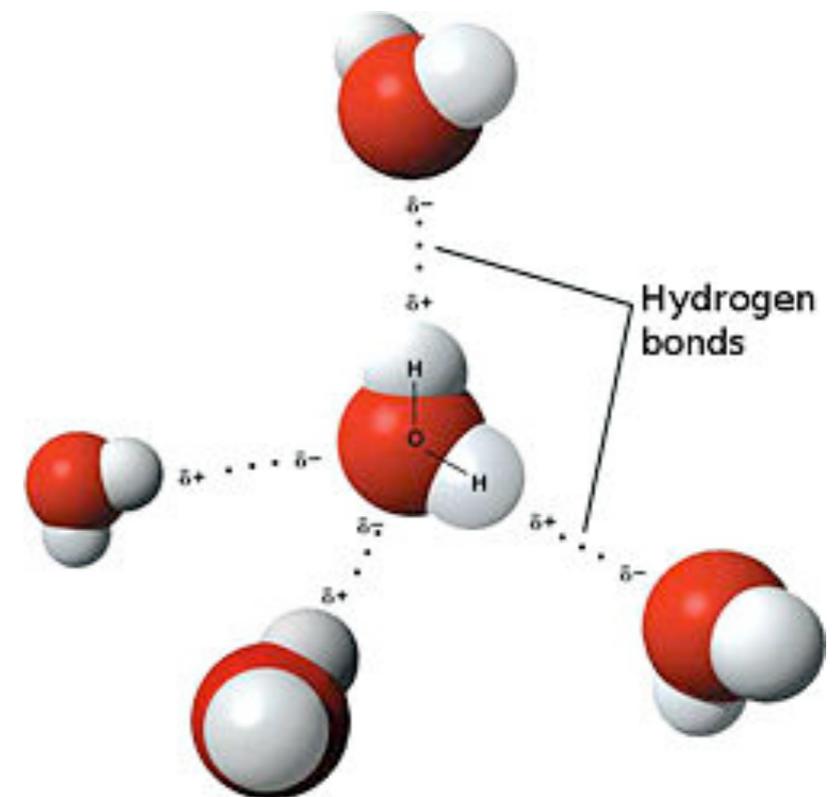
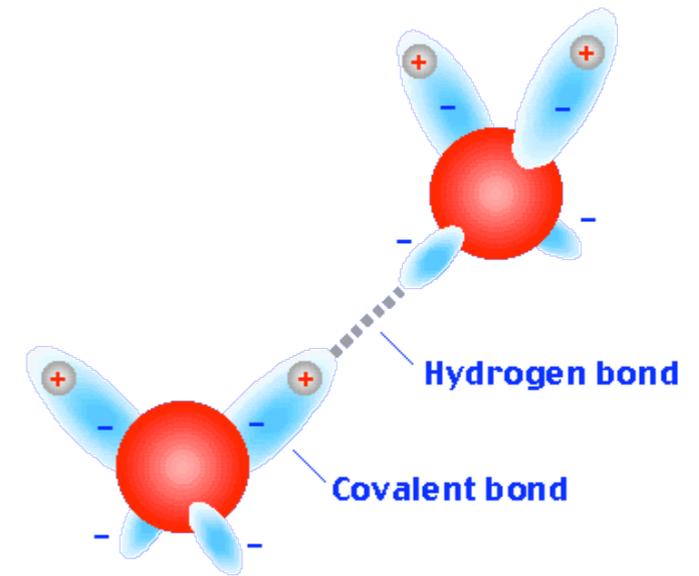
Legame fra molecole che si forma fra atomi elettronegativi (O, N, e Cl) di una molecola e un' atomo di idrogeno dell'altra.

L'interazione e' di tipo dipolo-dipolo

E' un legame relativamente forte perche':

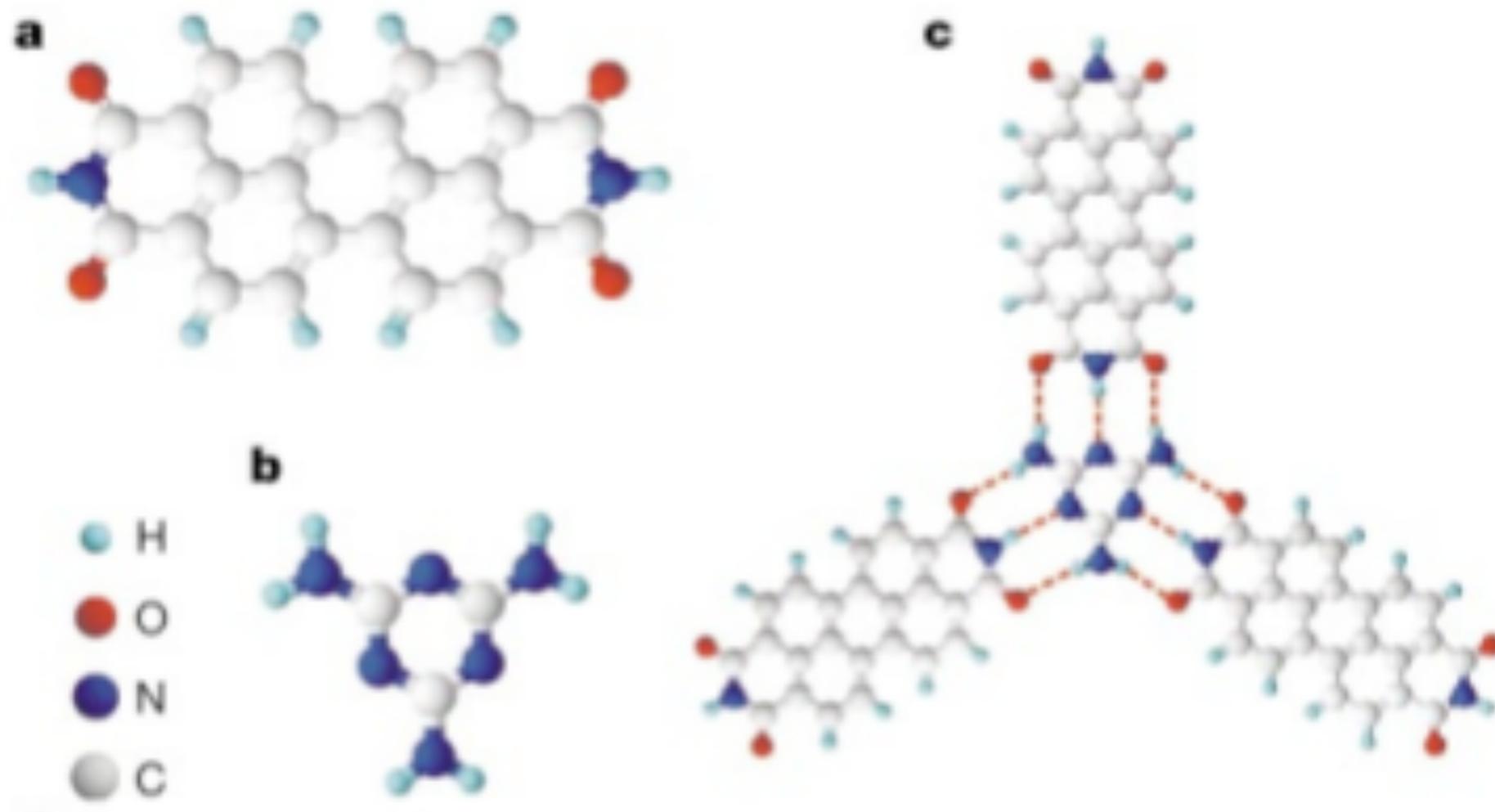
1. atomi elettronegativi: dipoli grandi
2. raggio H piccolo: distanze piccole

legame	dipolo (D)
C-H+	0.4
O-H+	1.51
N-H+	1.31
F-H+	1.94



Legame H e self-assembling

perylene tetra-carboxylic di-imide (PTCDI);



melamine

Supramolecular surface assembling

Formazione di un network ordinato a lungo raggio caratterizzato da 'pori' nanometrici

Evaporazione di C₆₀: cluster di 7 molecole (eptameri) in ciascun poro

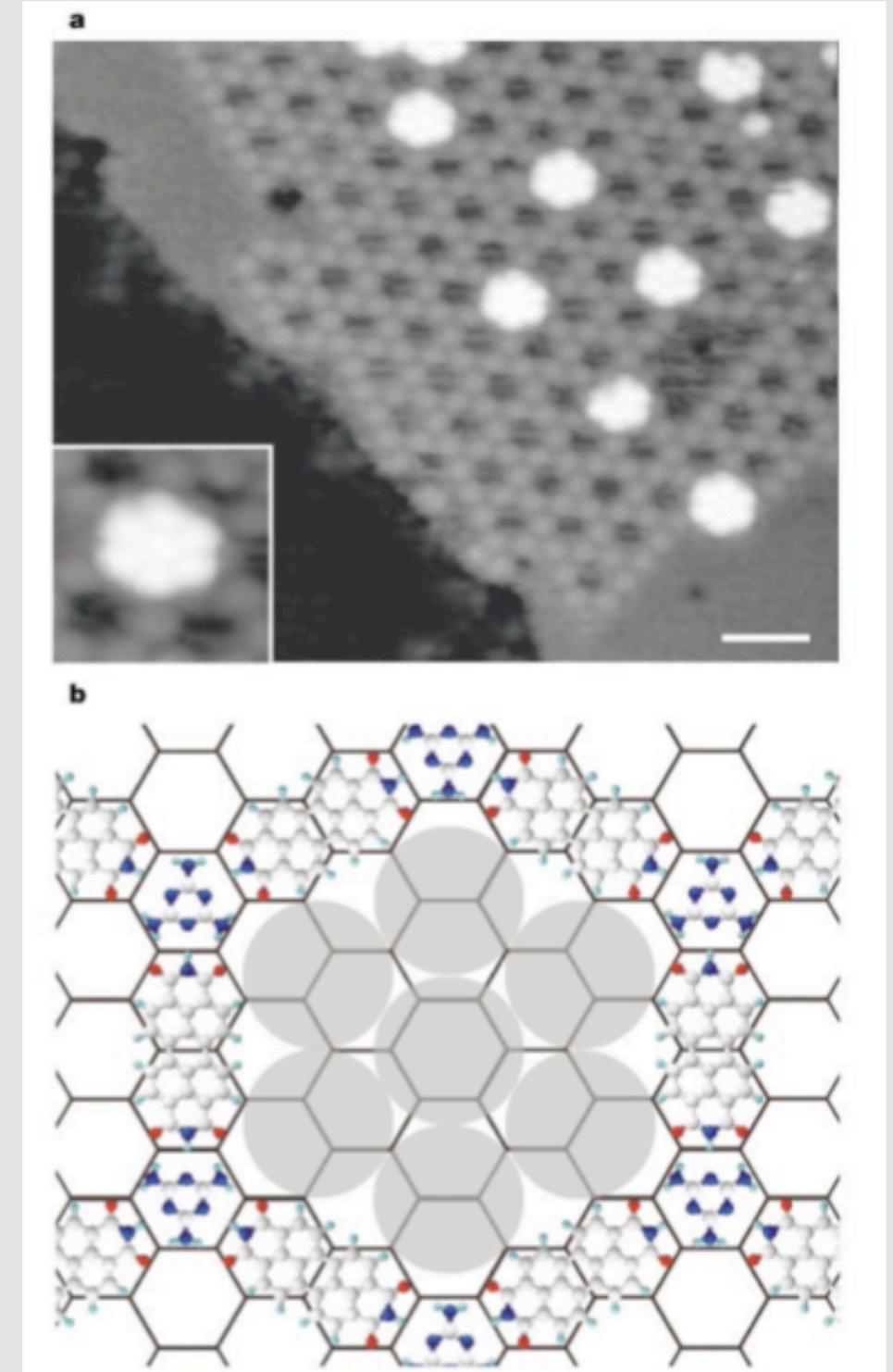
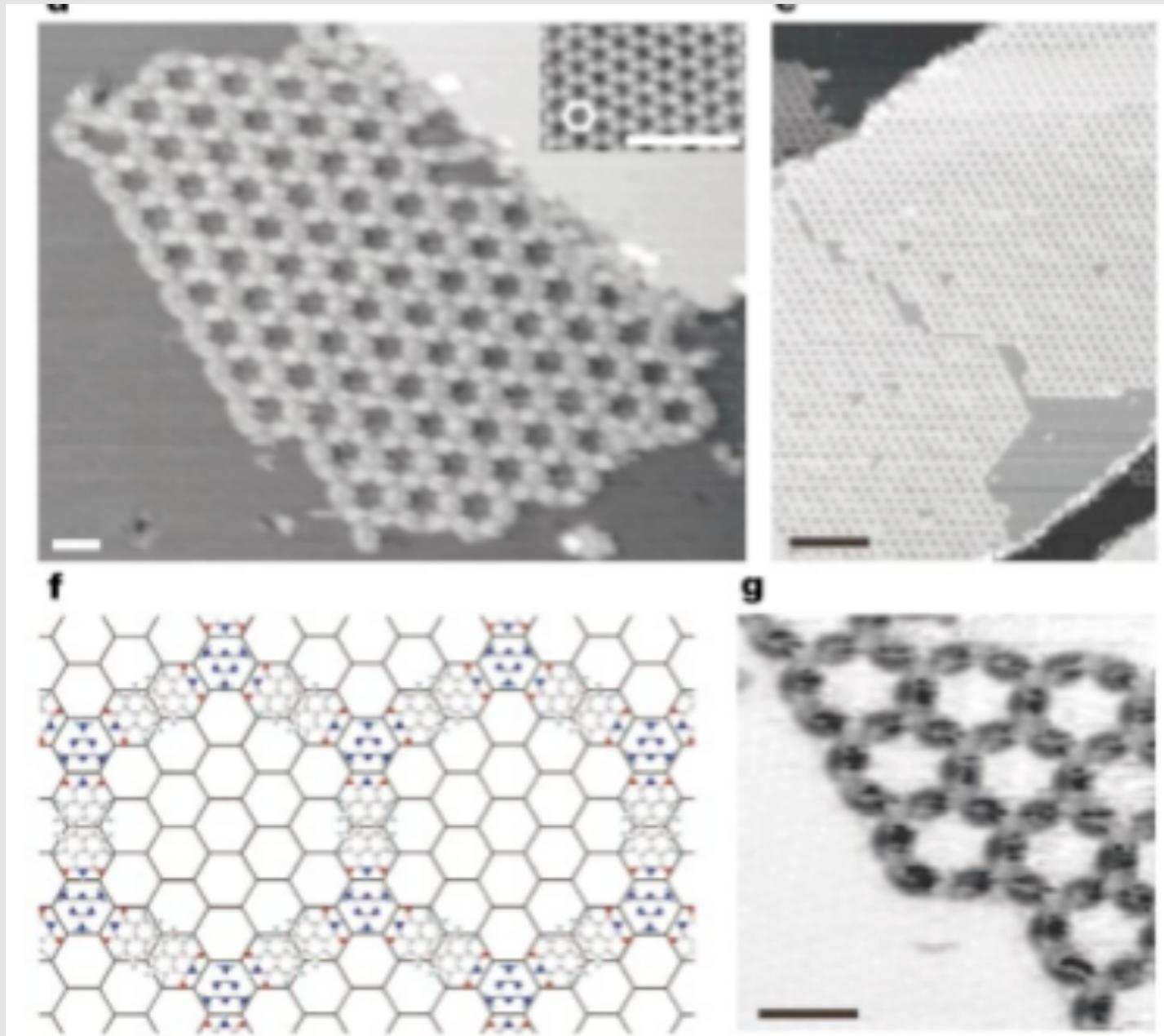


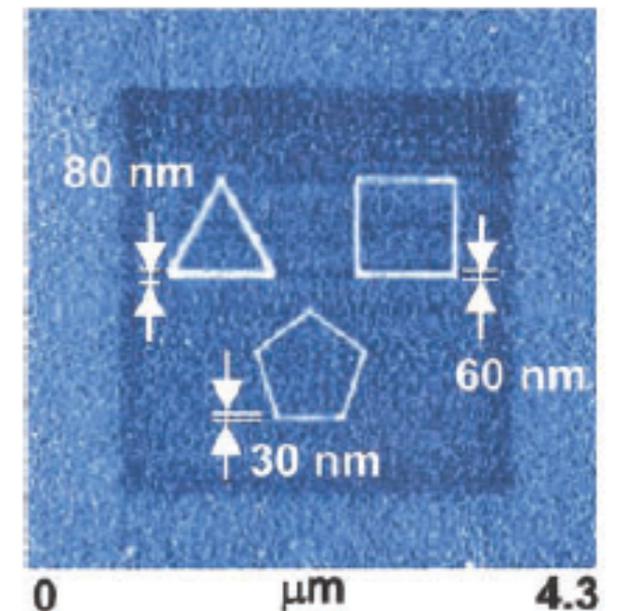
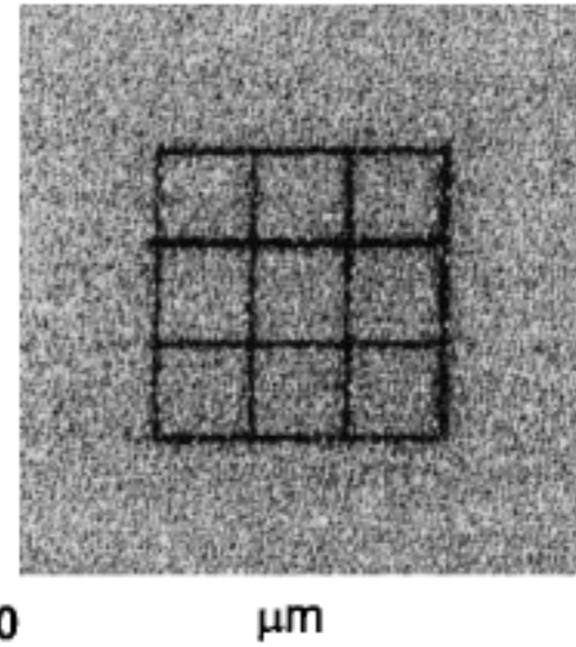
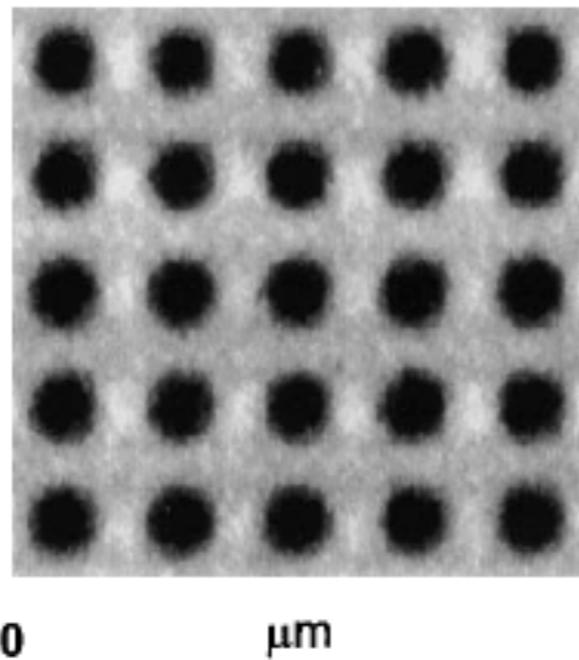
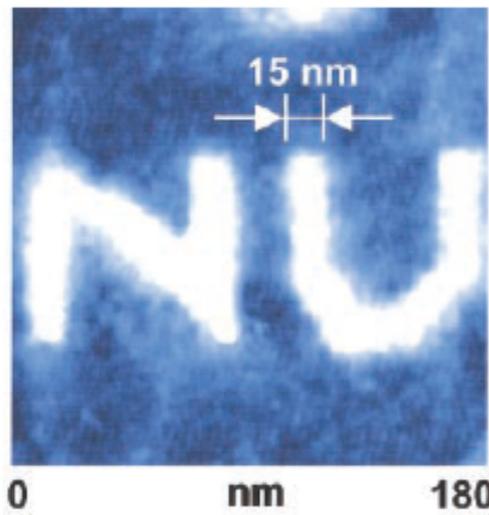
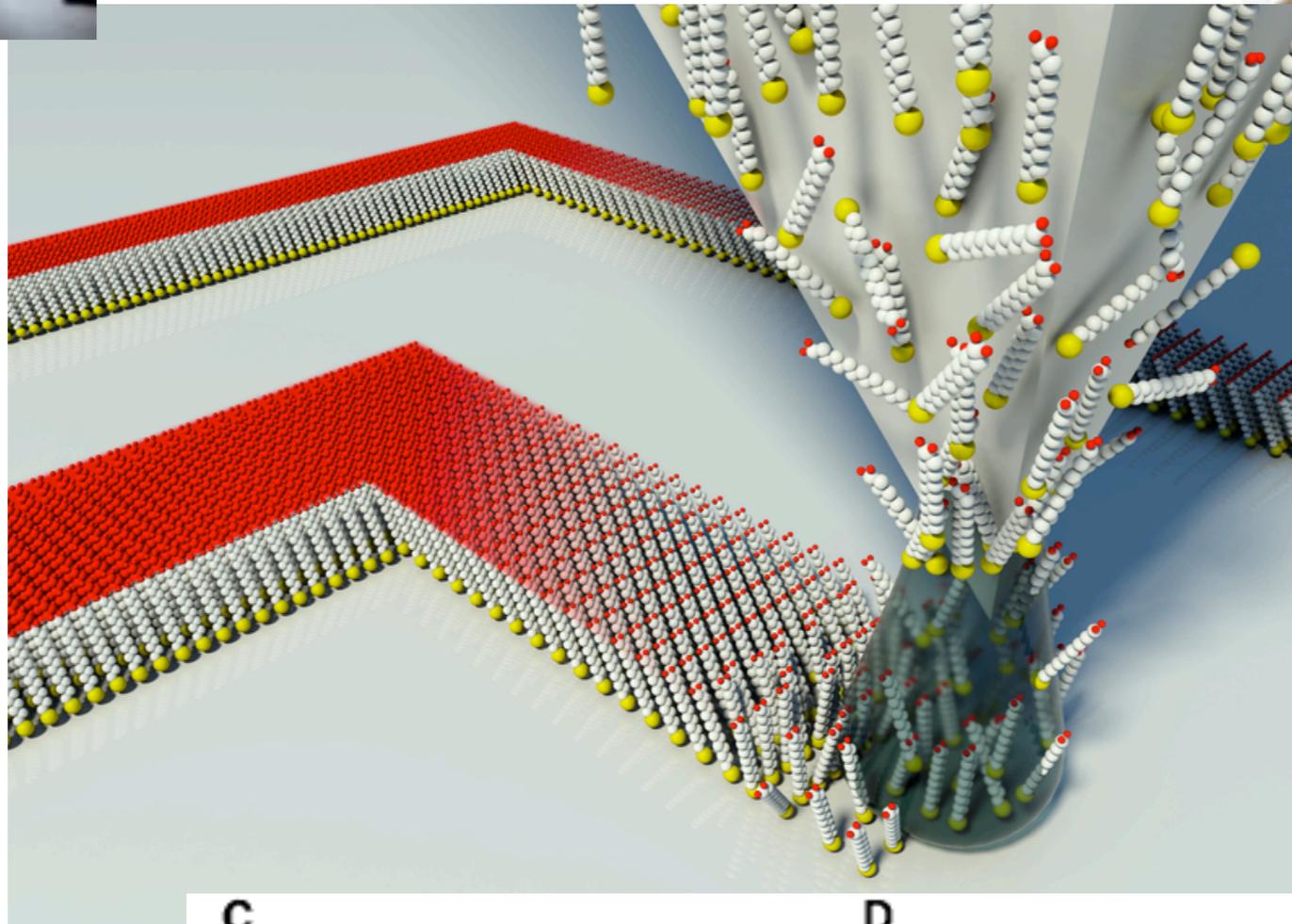
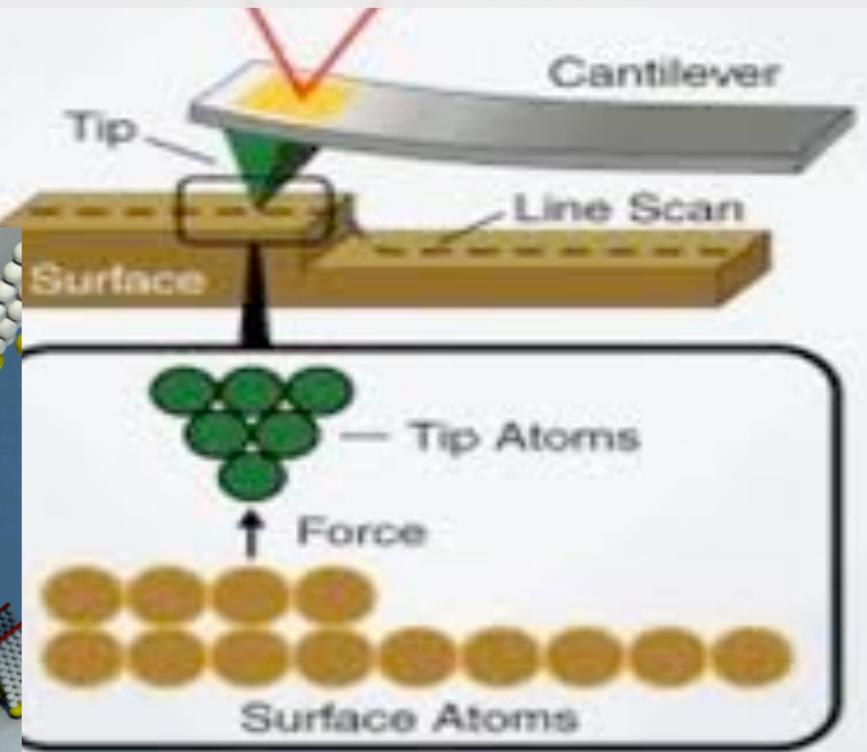
Figure 2 Images of C₆₀ heptamers trapped within the 'nanoscale vessels'. **a**, STM image (-2 V, 0.1 nA) of C₆₀ heptamers on a PTCDI-melamine network. Inset, high-resolution view showing an individual cluster. Scale bar, 5 nm. **b**, Schematic diagram of a C₆₀ heptamer.



"Dip-Pen" Nanolithography

Richard D. Piner, Jin Zhu, Feng Xu, Seunghun Hong,
Chad A. Mirkin*

Atomic Force Microscope

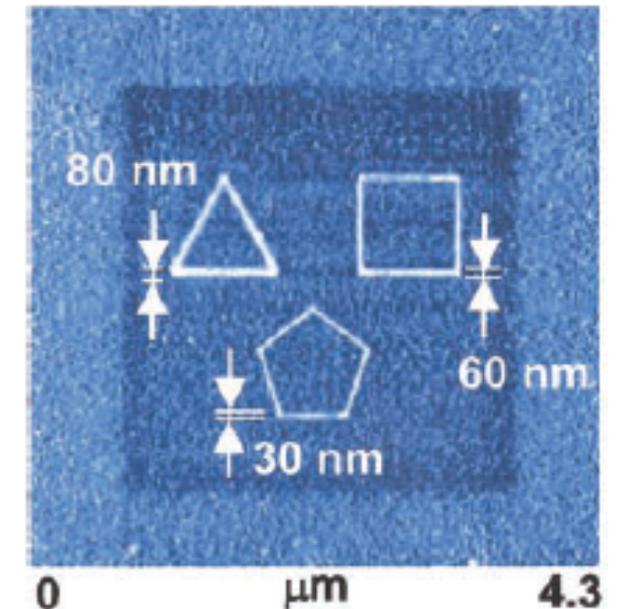
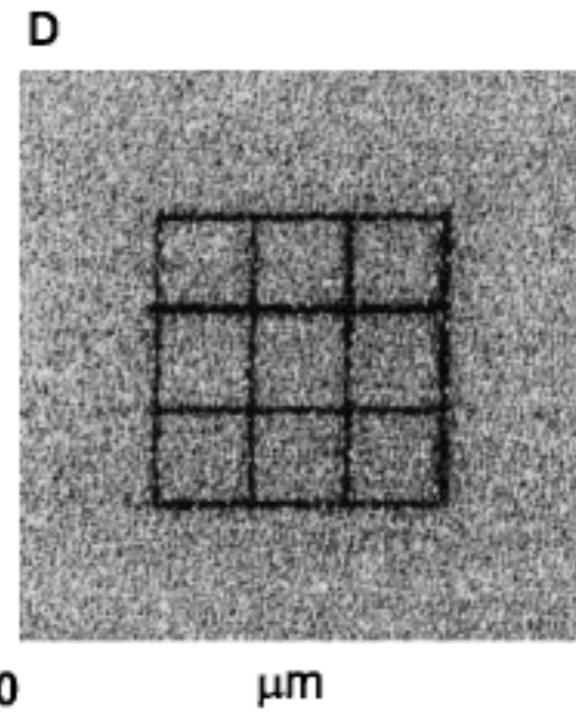
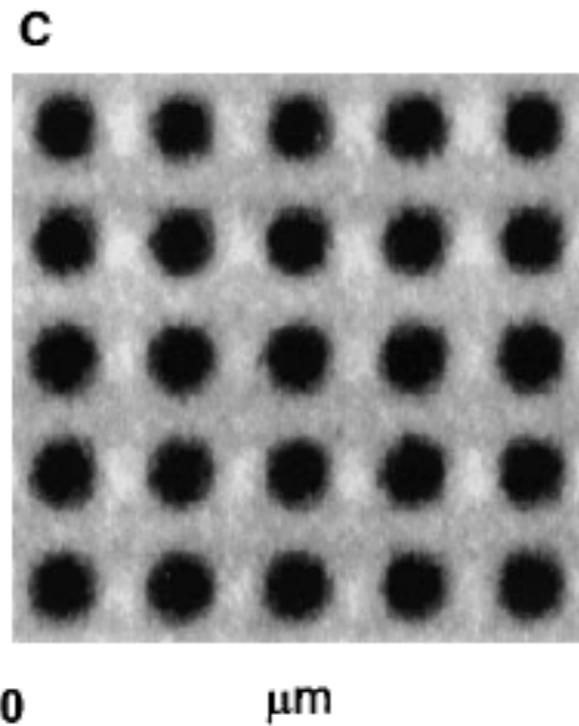
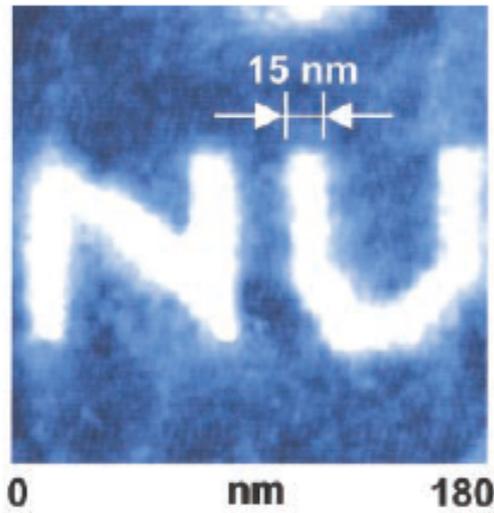
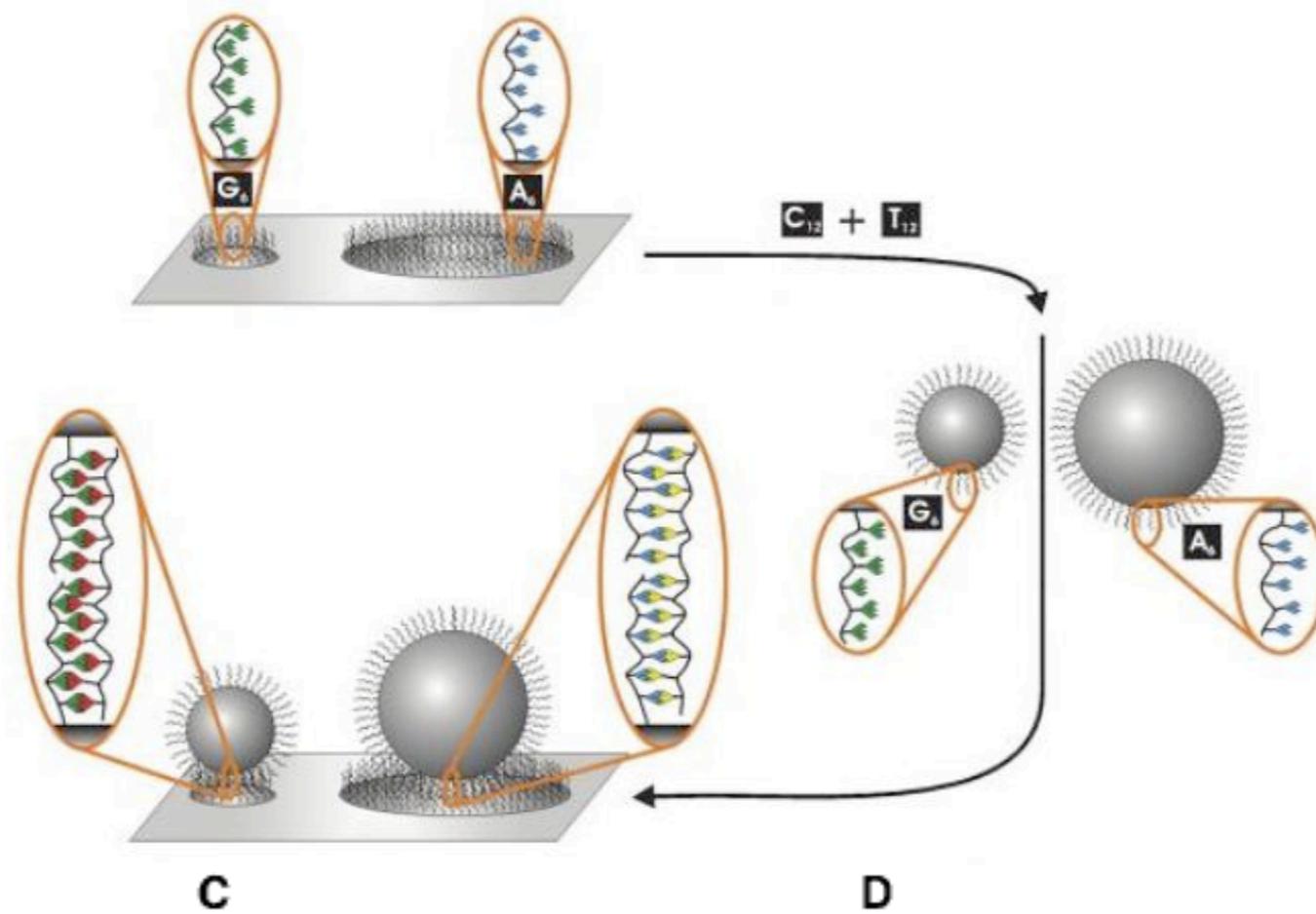
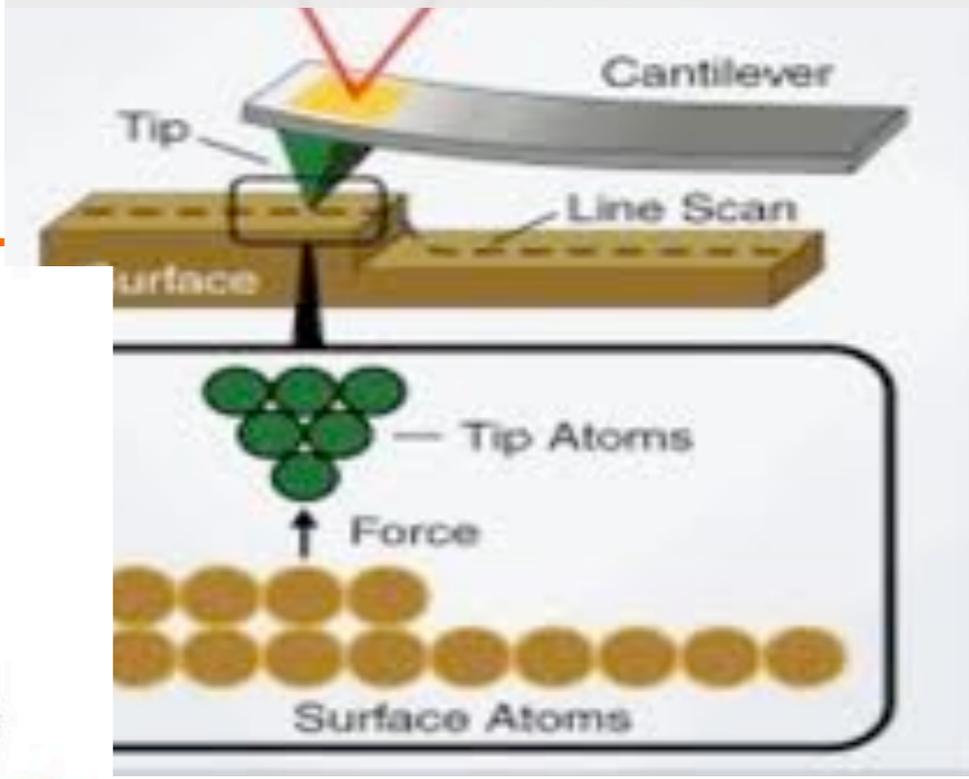




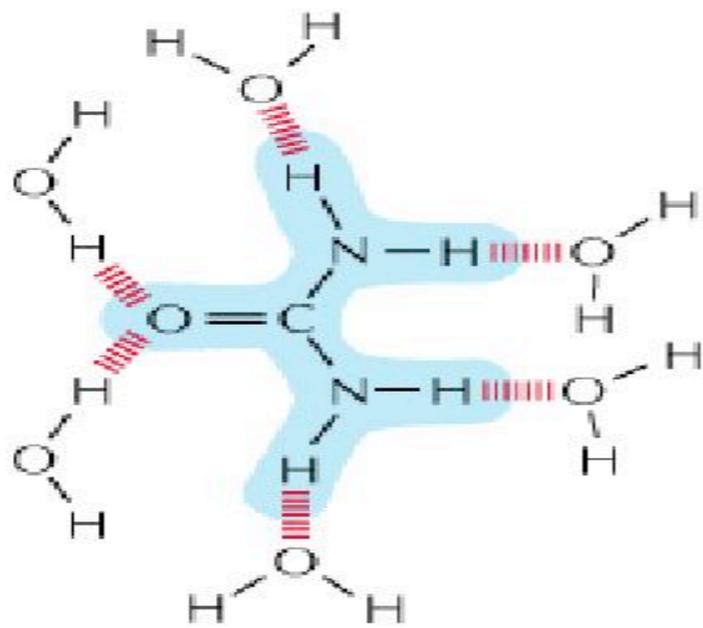
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Atomic Force Microscope



Molecole idrofiliche



≥ 50

Molecole che sono in grado di formare legami idrogeno (contengono gruppi polari, atomi elettronegativi...)

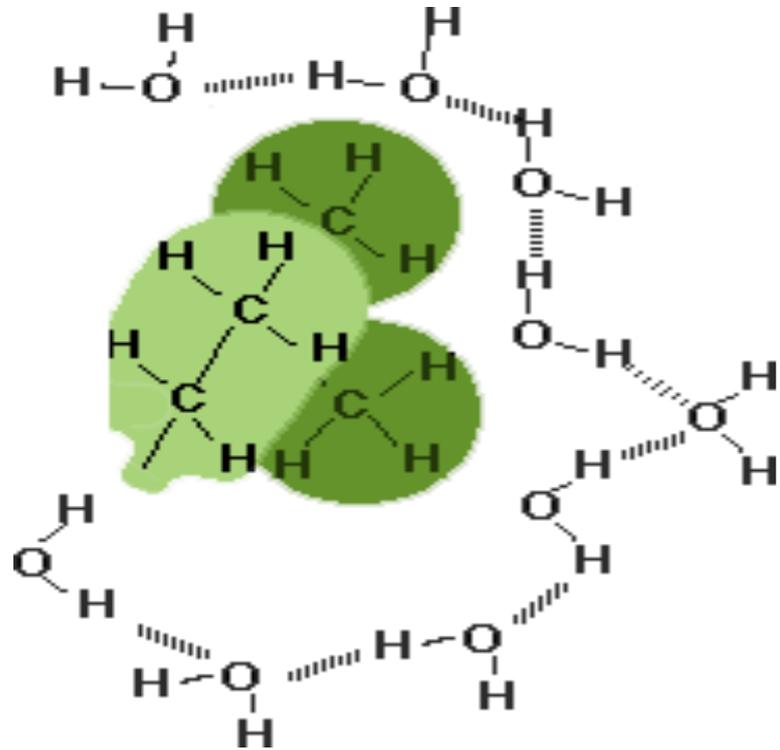
Queste molecole sono solubili in acqua (superfici idrofiliche si bagnano)

Cio' che determina la solubilita' e' principalmente il **contributo entropico**:

la possibilita' di formare nuovi legami idrogeno aumenta le possibili configurazioni delle molecole di acqua  aumenta l'entropia (Si parla di agenti **caotropici**)

Molecole idrofobiche

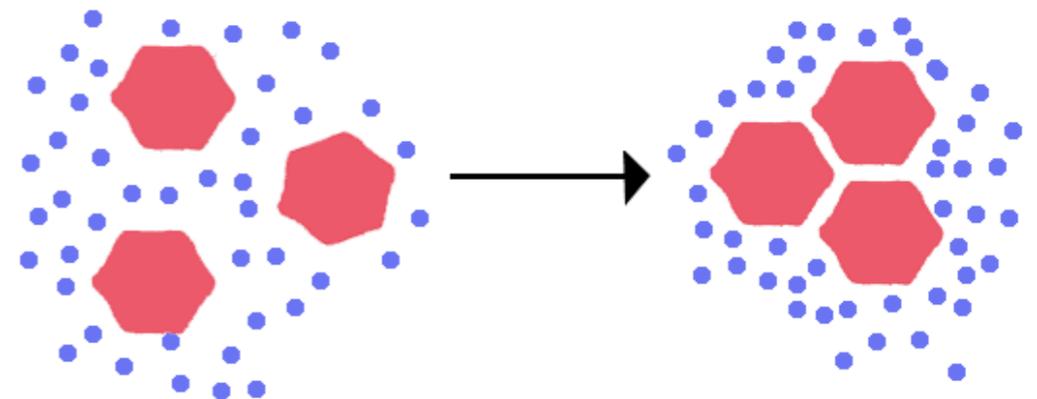
molecole NON POLARI, che non sono in grado di formare legami H



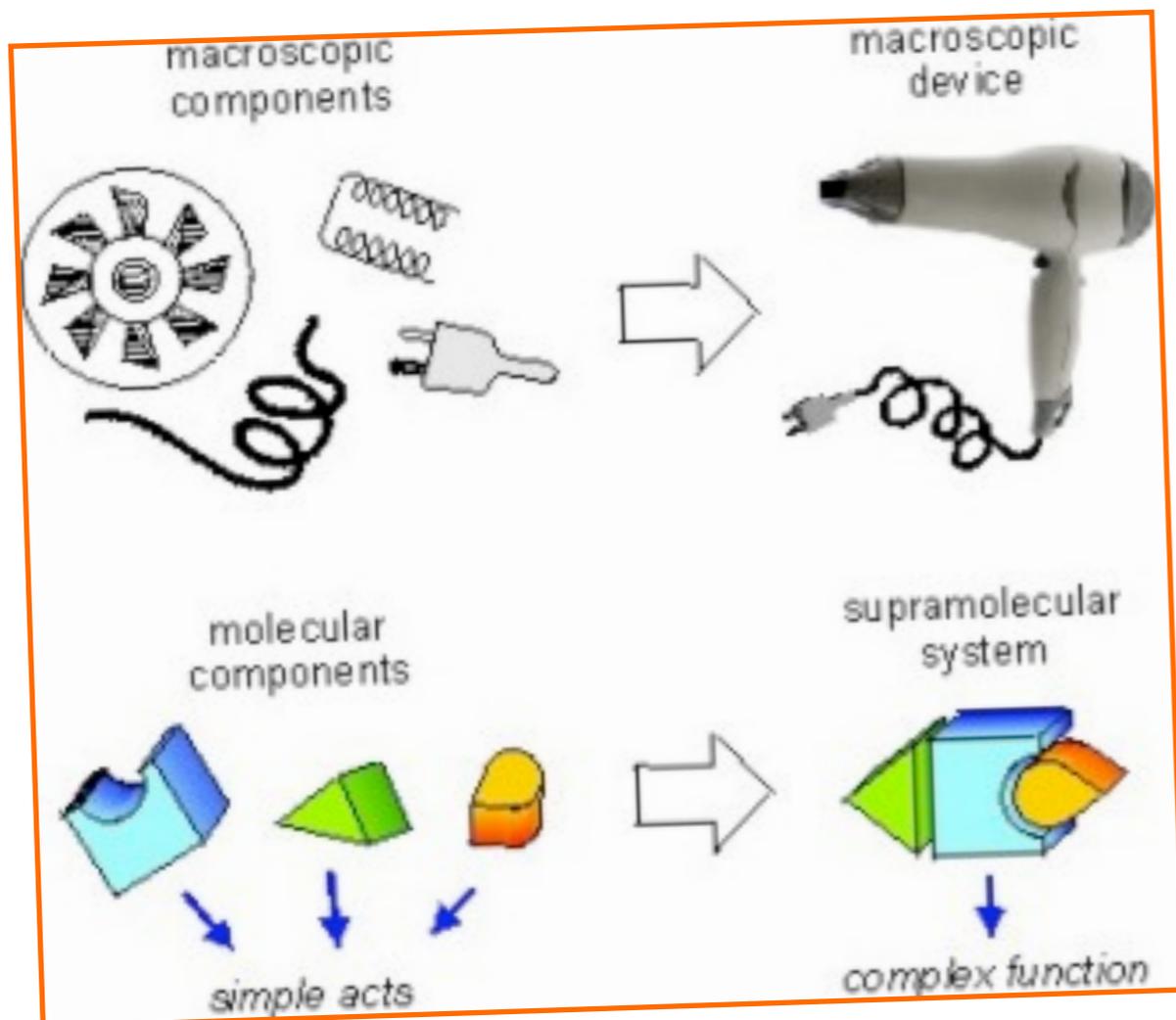
- La presenza di molecole non polari altera la struttura 3D del network di legami idrogeno dell'acqua:
- Questo ha però un costo ENTROPICO

L'interazione idrofobica tiene unite le molecole:
Gruppi idrofobici circondati da acqua tenderanno a coalescere in modo da ridurre la loro superficie di contatto con l'acqua. La coalescenza è favorita entropicamente

- **molecole non solubili**
- **superfici idrofobiche non si bagnano (no-wetting)**



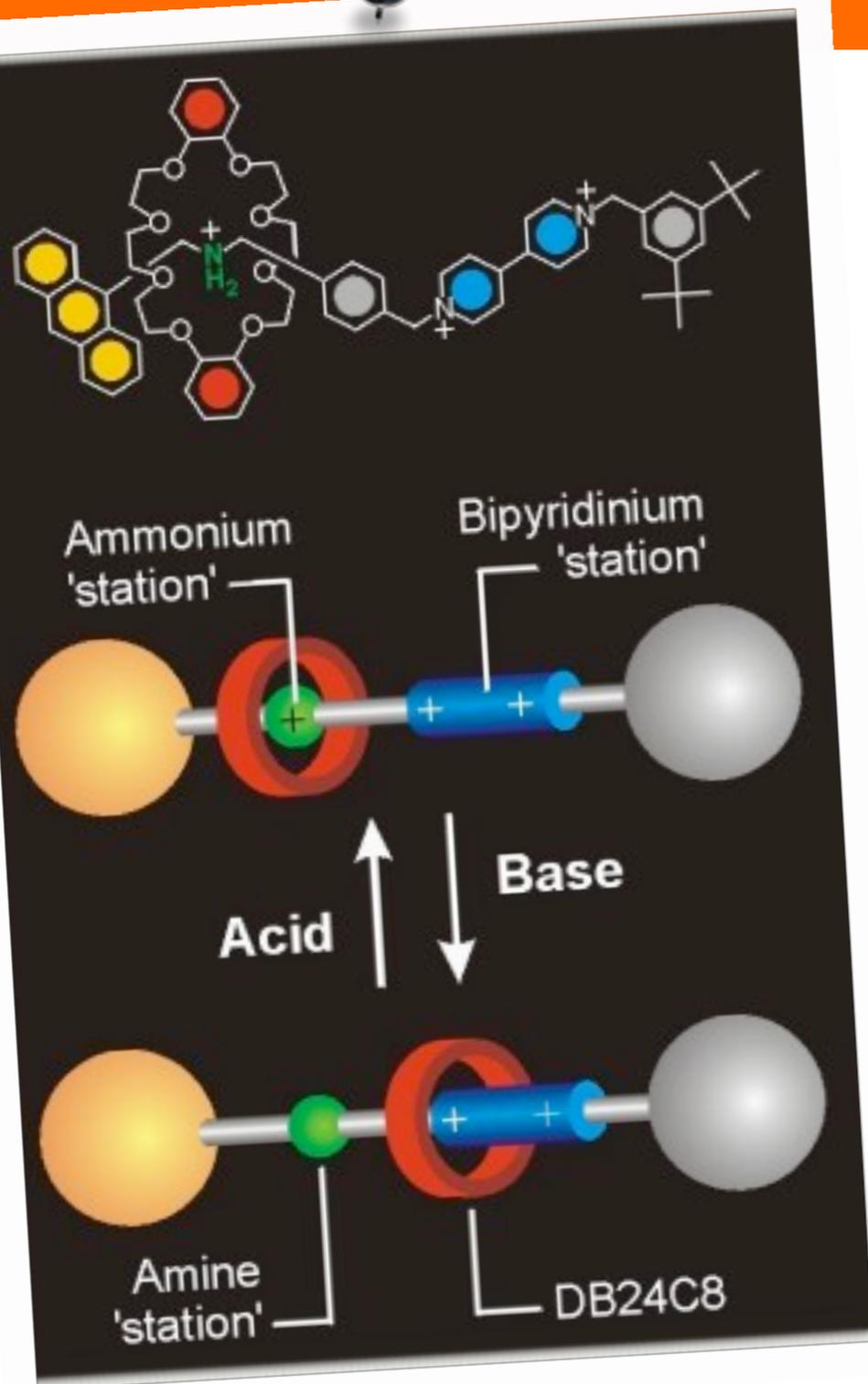
I sistemi supramolecolari



- Per costruire un dispositivo nanoscopico posso utilizzare singole molecole come 'pezzi' di un meccano

Affinche' il dispositivo faccia qualcosa, occorre che i singoli pezzi, sottoposti ad uno stimolo, si possano muovere:
legami non-covalenti, posizioni metastabili

Rotaxani

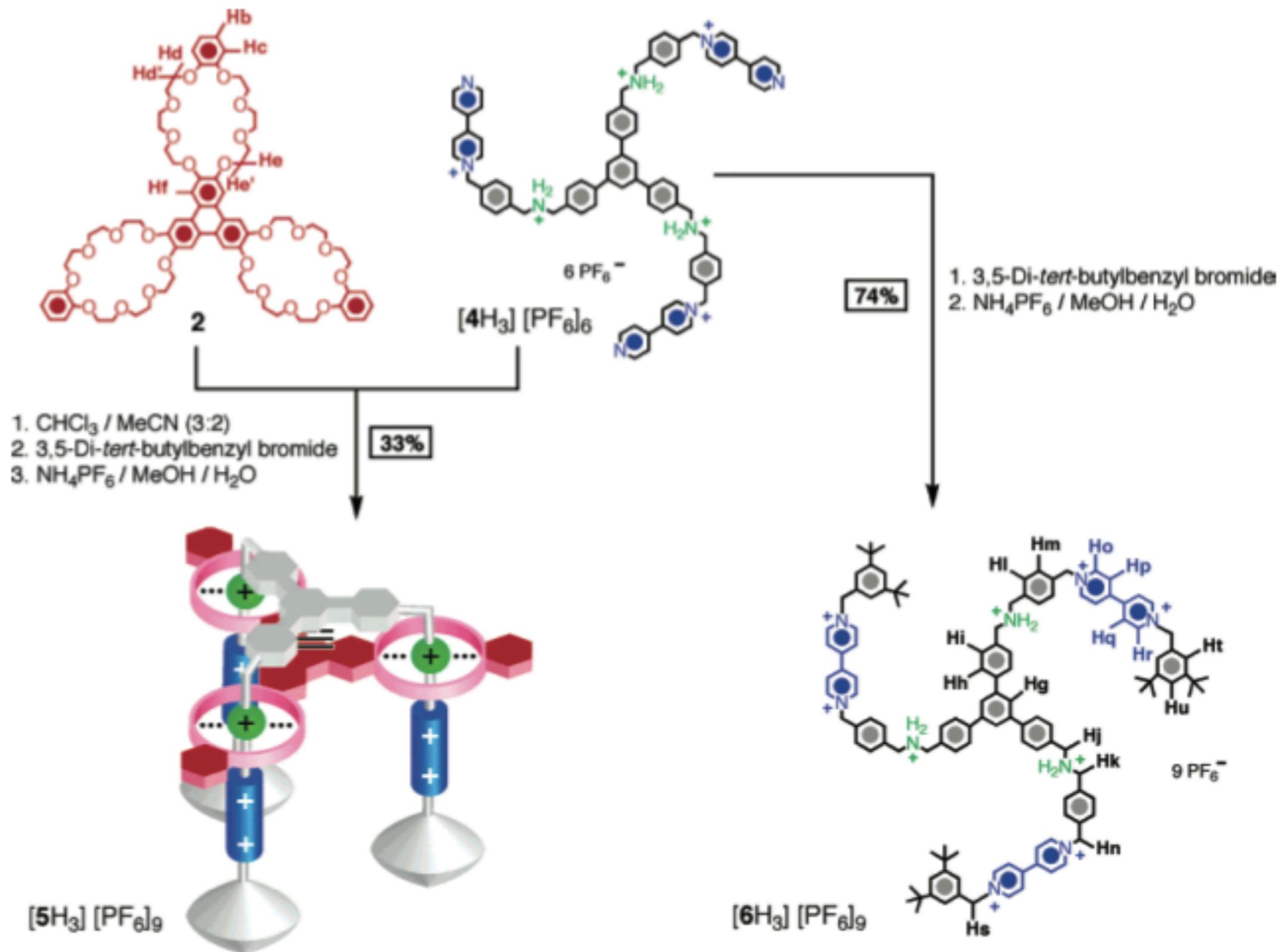


- La **molecola rossa** ad anello puo' interagire con la postazione **verde** o con quella **blu**
- Uno stimolo esterno (per es. pH o luce) puo' accendere/spegnere l'interazione e fare in modo che l'anello si sposti

Movimento nanometrico comandato da uno stimolo esterno

Assemblaggio di una macchina molecolare:

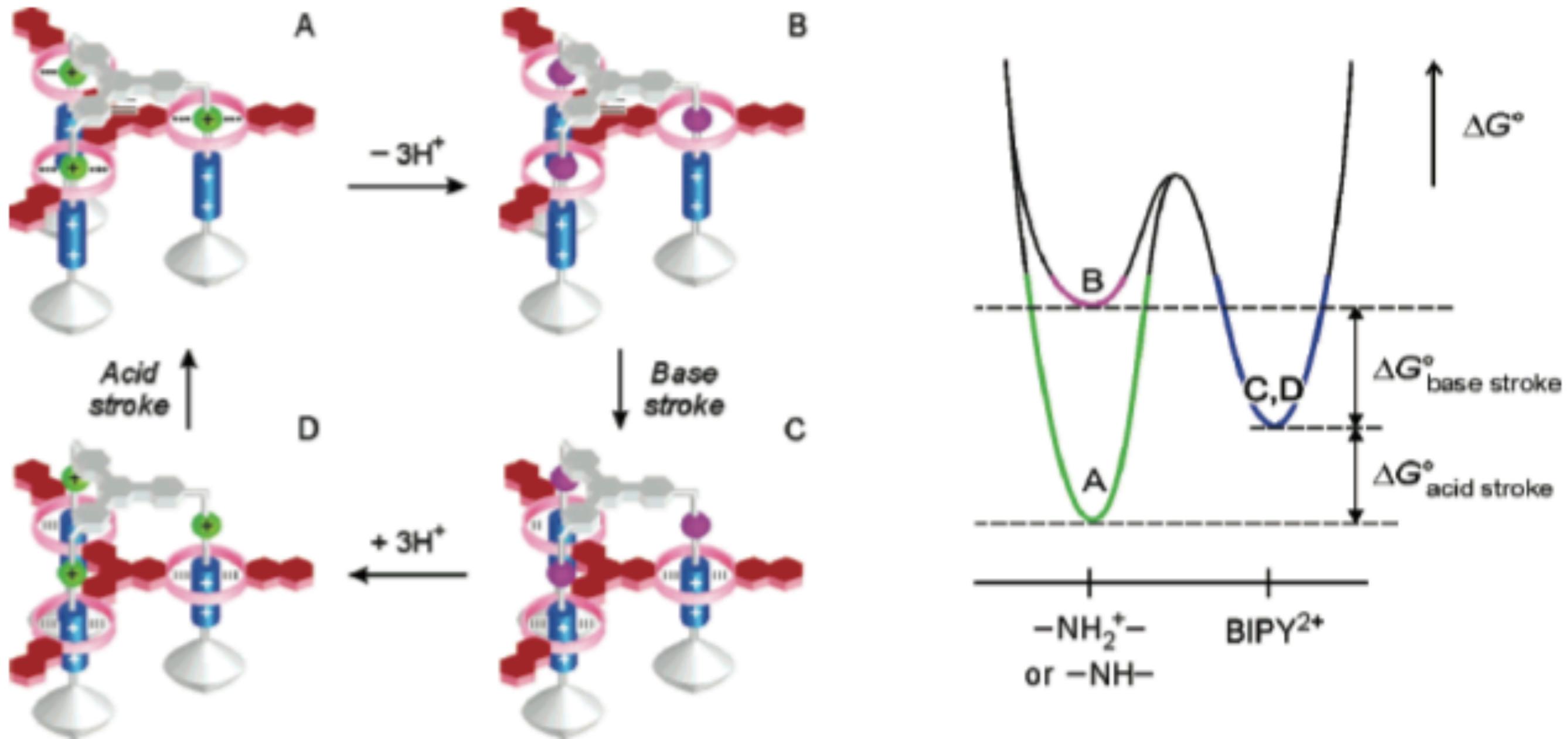
Scheme 2^a



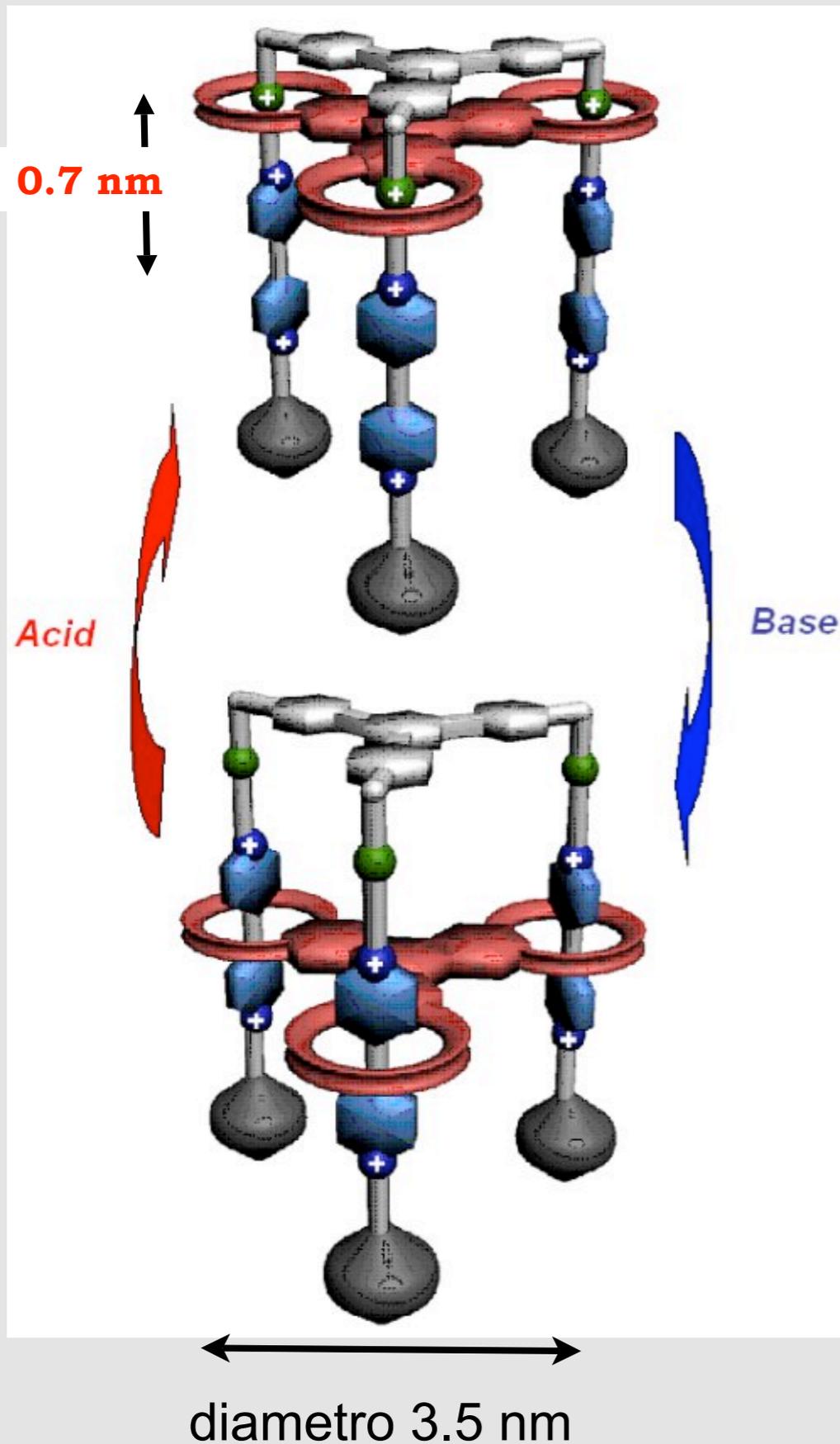
Stoddard (UCLA), Balzerani, Credi (Ciamician Bo) et al.

Energia Potenziale

4. Base–Acid-Controlled Mechanical Switching in the Molecular Elevators^a



Ascensore molecolare



Modificando la soluzione (acida/base) la piattaforma sale/scende di 0.7 nm, sviluppando una forza pari a 200 pN

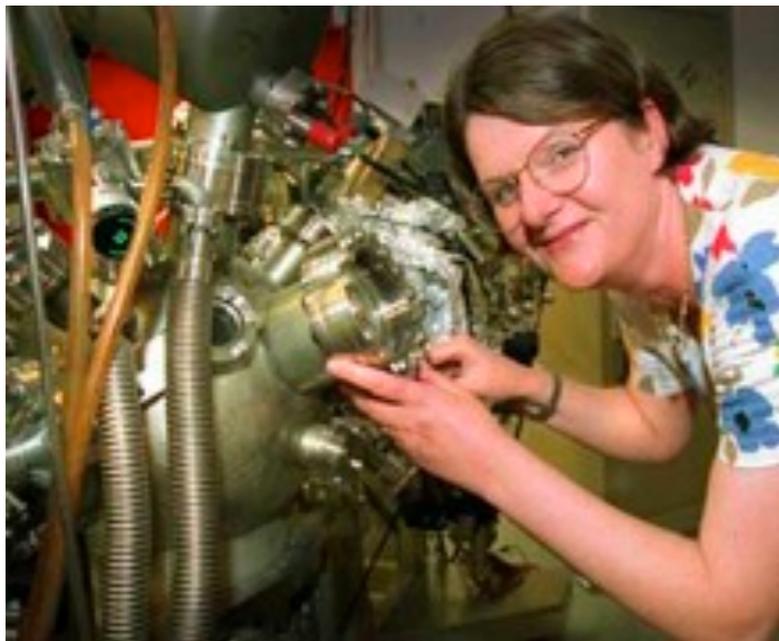
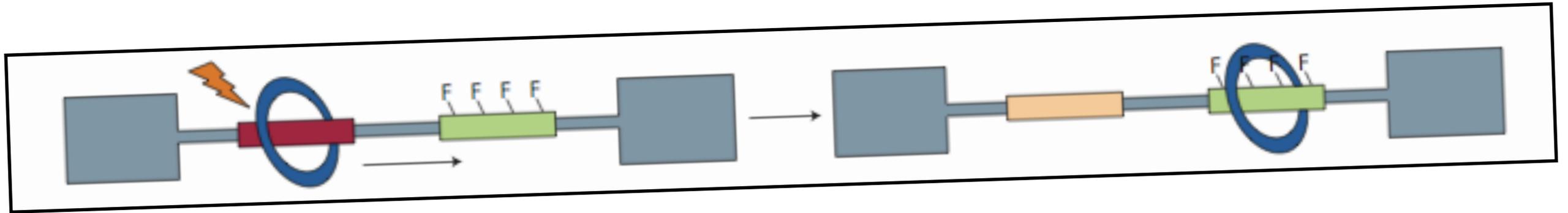
Possibile applicazione: utilizzo per il rilascio lento di farmaci:

- Se si riesce a disporre questo sistema su una superficie di silicio nanoporoso



rilascio controllato di molecole che si trovino dentro i nanopori

modifica dell'idrofobicità di una superficie

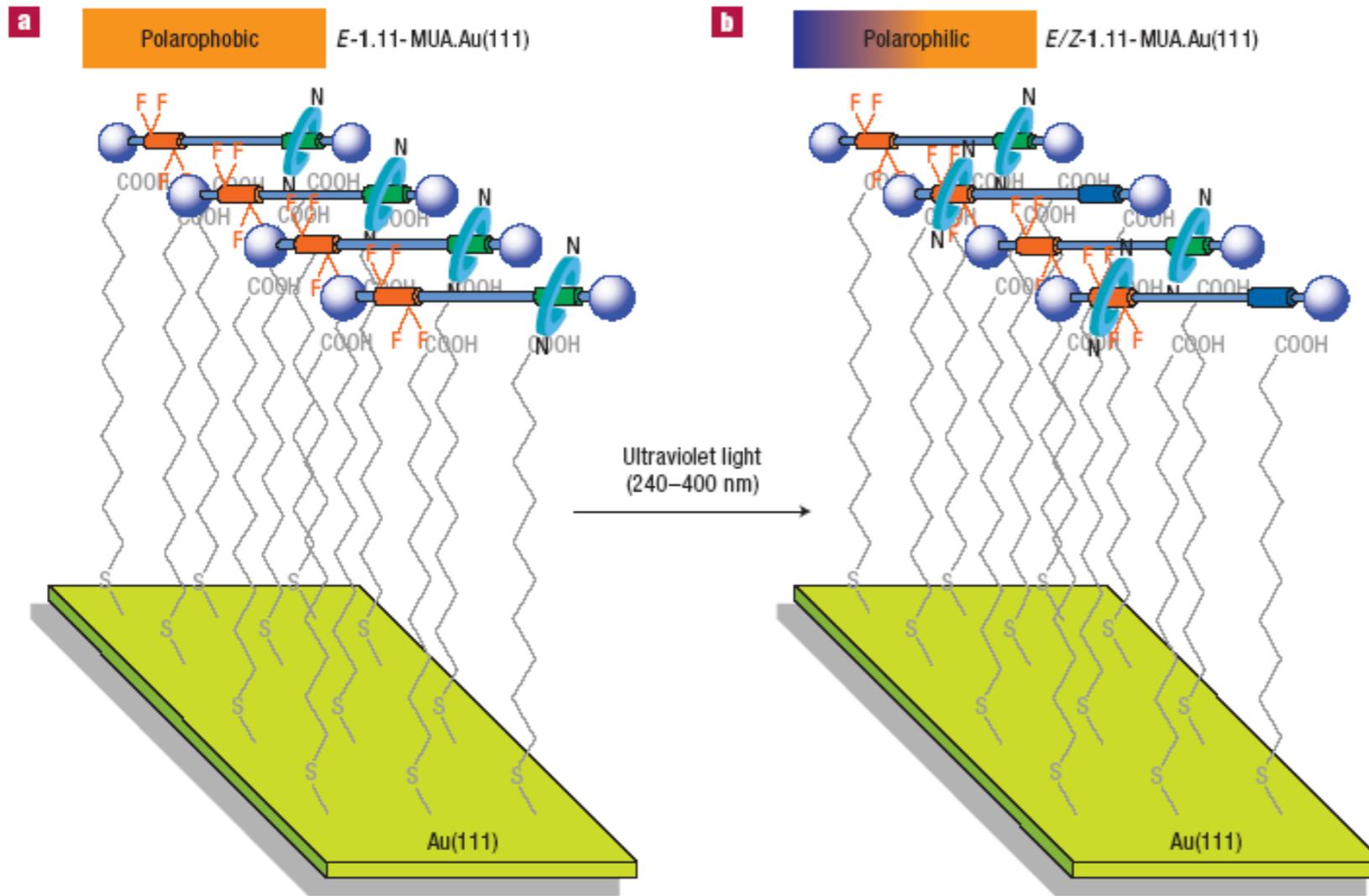


P.Rudolf University of Groningen
V. Balzerani Università di Bologna

Macroscopic transport by synthetic molecular machines

nature materials | VOL. 4 | SEPTEMBER 2005 | w

JOSÉ BERNÁ¹, DAVID A. LEIGH^{1*}, MONIKA LUBOMSKA², SANDRA M. MENDOZA², EMILIO M. PÉREZ¹, PETRA RUDOLF^{2*}, GILBERTO TEOBALDI³ AND FRANCESCO ZERBETTO^{3*}

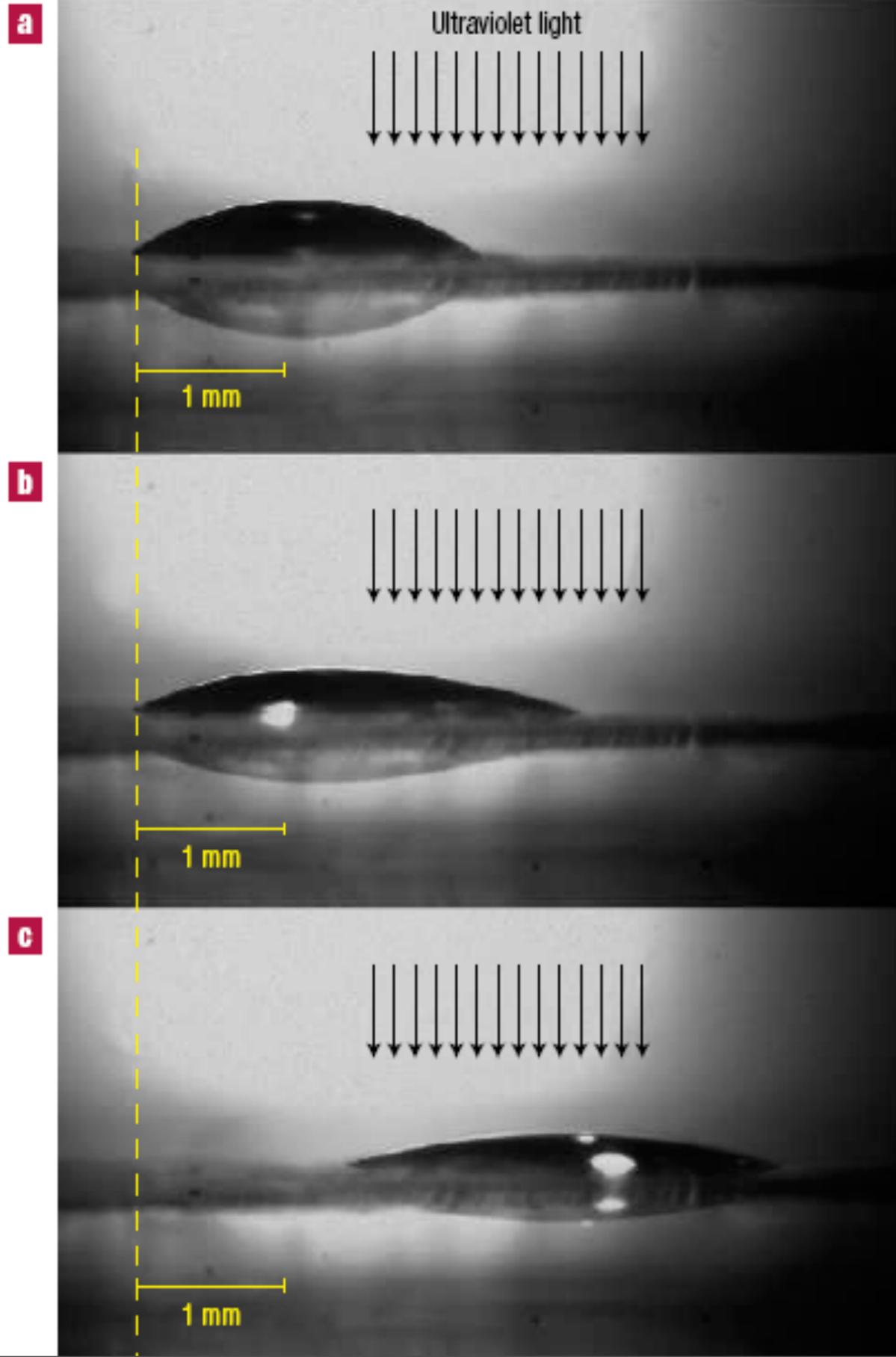


Misura dell'angolo di contatto di diversi solventi prima/dopo avere irradiato la superficie:

La superficie 'illuminata' diventa polarofila
l'angolo di contatto \rightarrow diminuisce

	θ (°)*	
	Deposited before ultraviolet irradiation of surface	Deposited after ultraviolet irradiation of surface
Diiodomethane	35	13
Water	55	45
Formamide	40	31
Ethylene glycol	48	40
Bromoform	18	12
Dimethylformamide	15	— [†]
Nitromethane	6 [†]	5 [†]
1,2-dibromoethane	8	— [†]

la goccia si muove verso la zona idrofilica



la goccia si muove verso la zona idrofilica

