



**The Abdus Salam
International Centre for Theoretical Physics**



2054-14

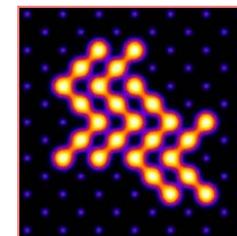
Structure and Dynamics of Hydrogen-Bonded Systems

26 - 27 October 2009

**Hydrogen bonding in bi-component supramolecular nanoporous networks
A combined STM and DFT study**

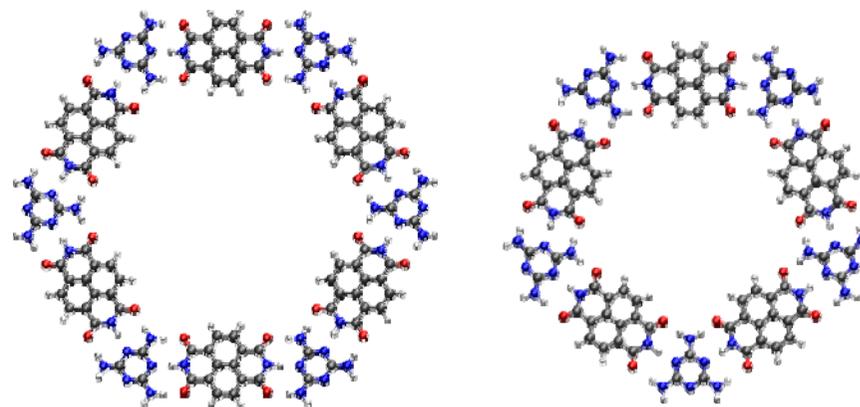
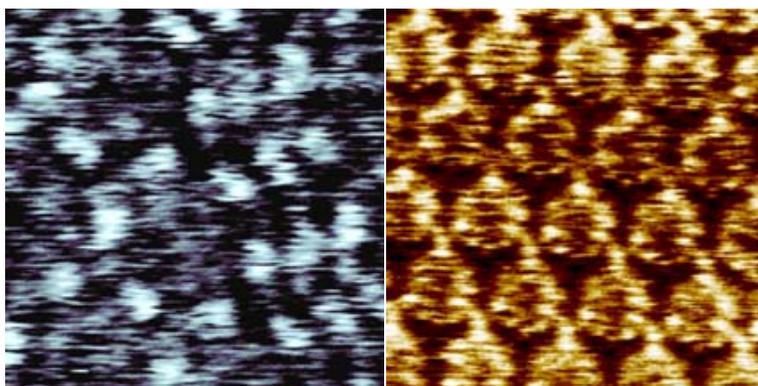
Jonas BJORK
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University of Liverpool, L15 0HH
Liverpool
U.K.*

PRAIRIES network



Hydrogen bonding in bi-component supramolecular nanoporous networks

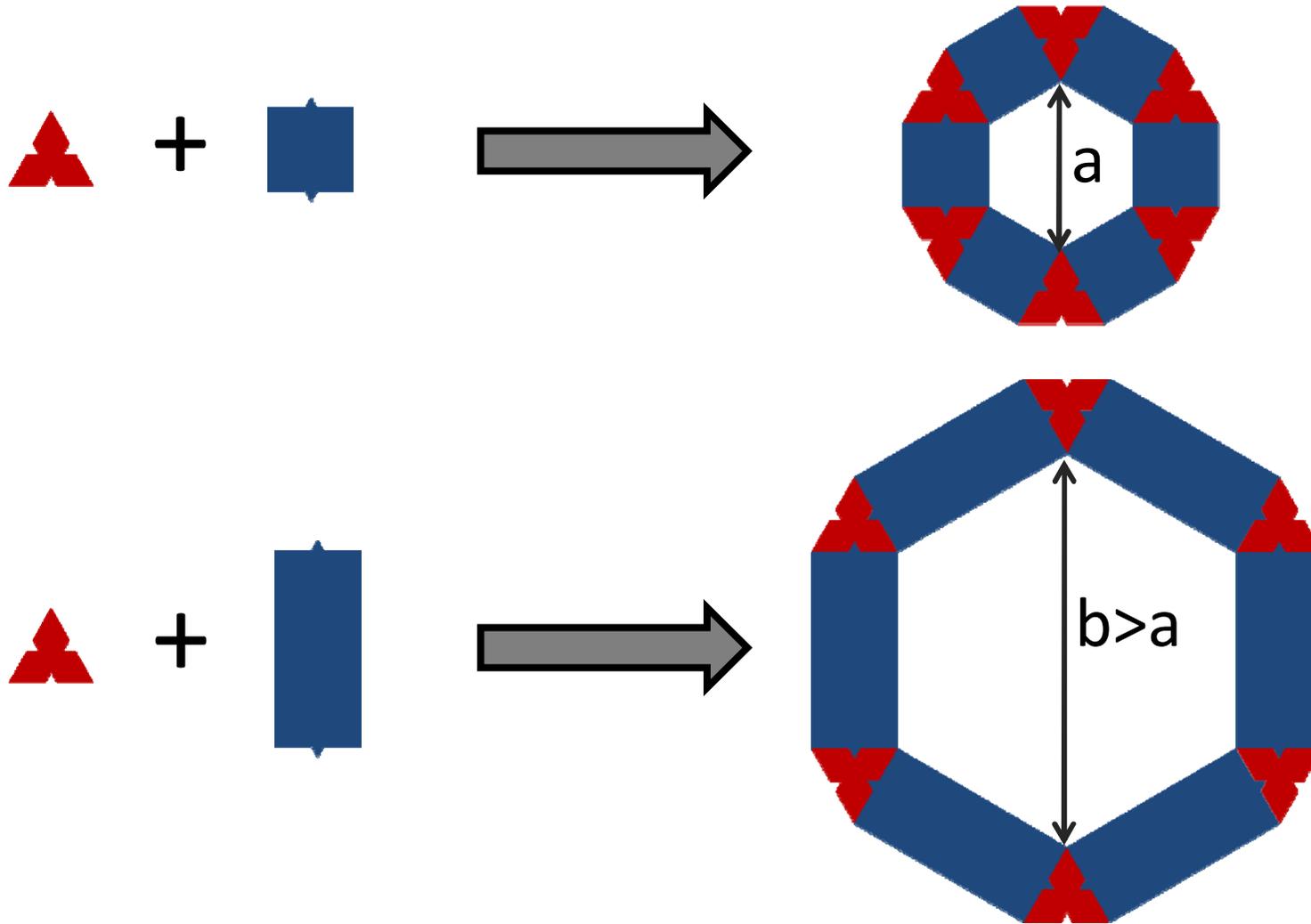
A combined STM and DFT study



JONAS BJÖRK

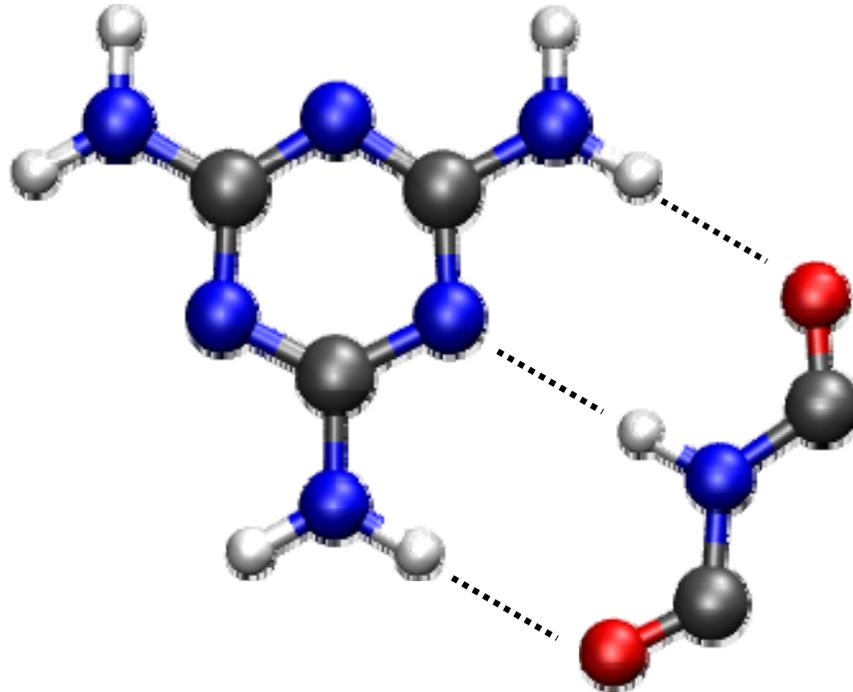
pcwww.liv.ac.uk/~bjork

Controlling the pore size



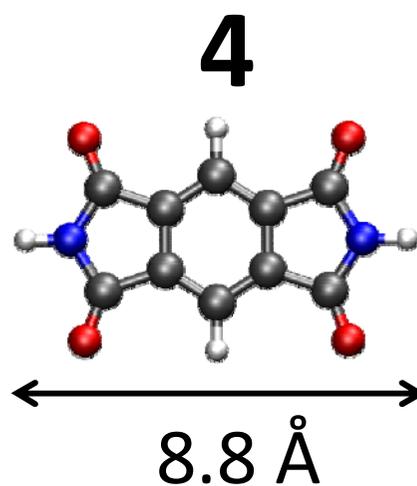
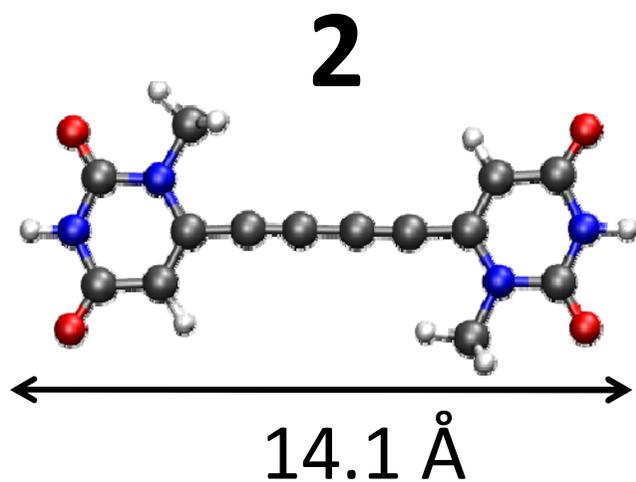
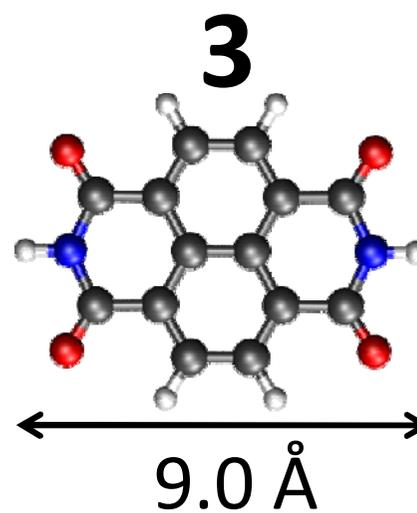
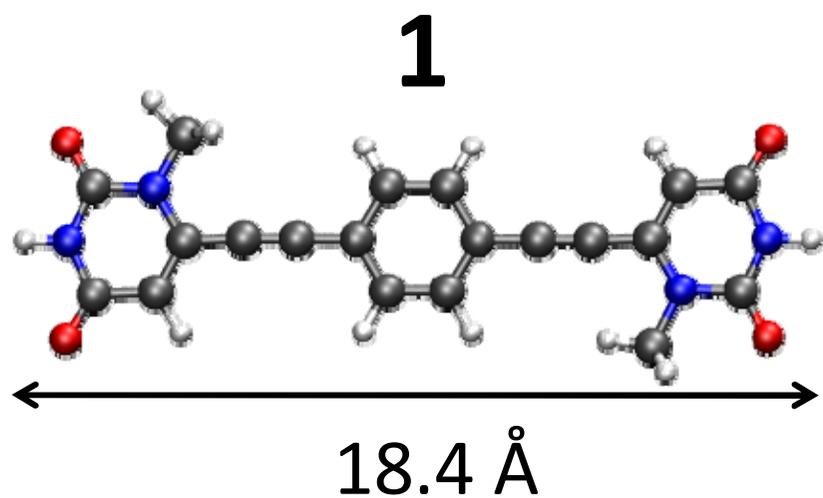
Connecting melamine with linkers

Hydrogen bond bridges

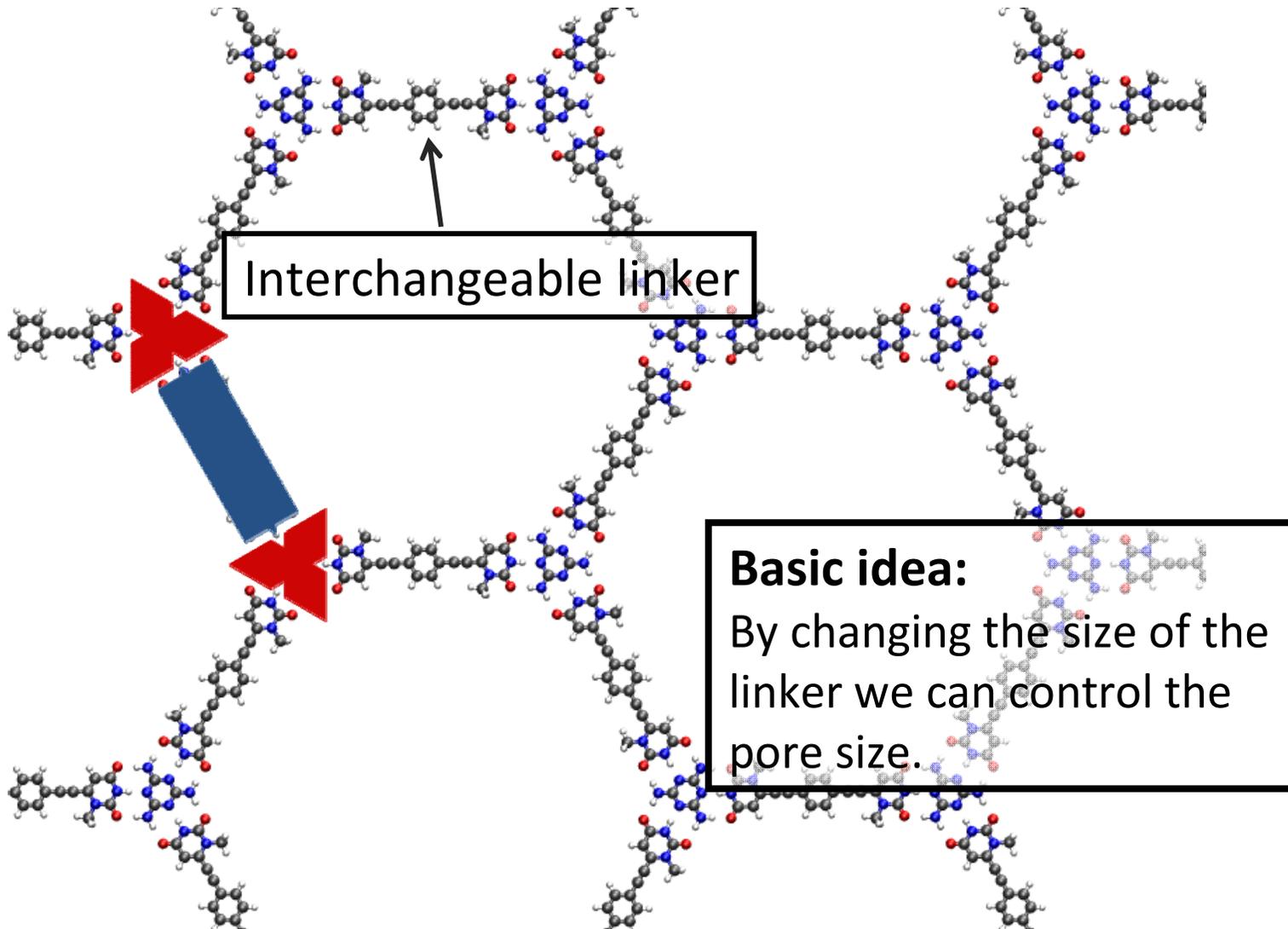


Triple hydrogen bonds between melamine and different linker modules.

Linker modules



Melamine + Linker module



Methods

STM

- Study the self-assembly of melamine blended with the linkers in solution and on graphite.
- Express the order of the different structures by Fourier transformations of the images.

DFT

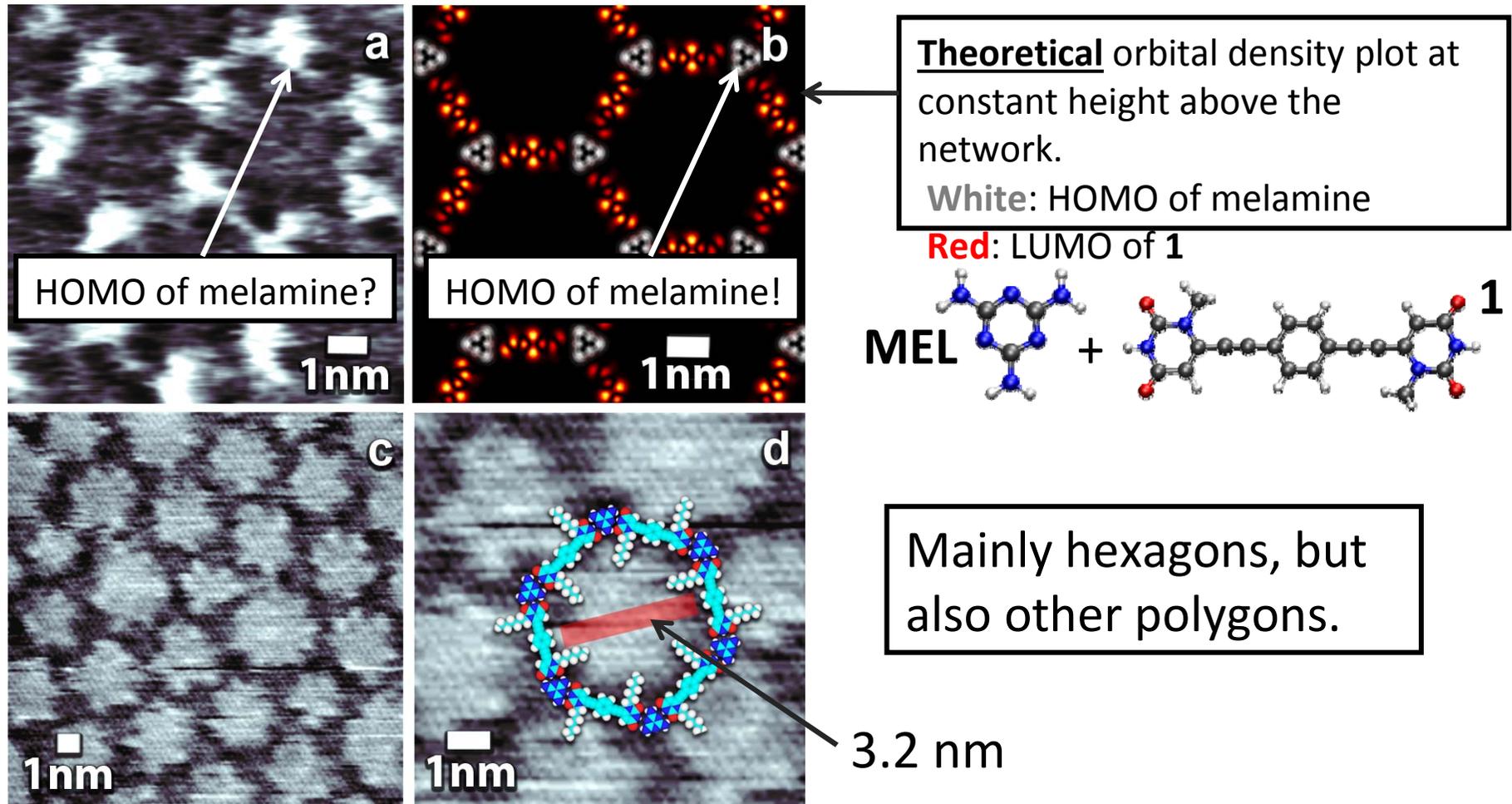
- Explain the observed variety of polygons/polymorphism.
- Role of length vs. rigidity
- Isolated networks

DFT details

- The VASP code with PAW-potentials
- PW91 XC-functional
- 400 eV cutoff energy
- All structures relaxed until forces on individual atoms were less than 0.01 eV/Å.

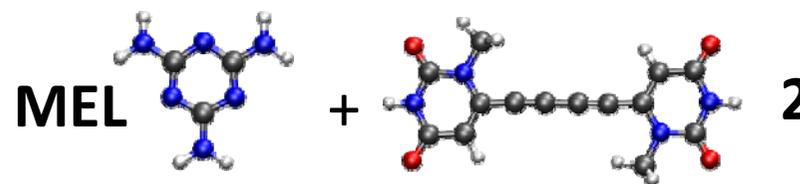
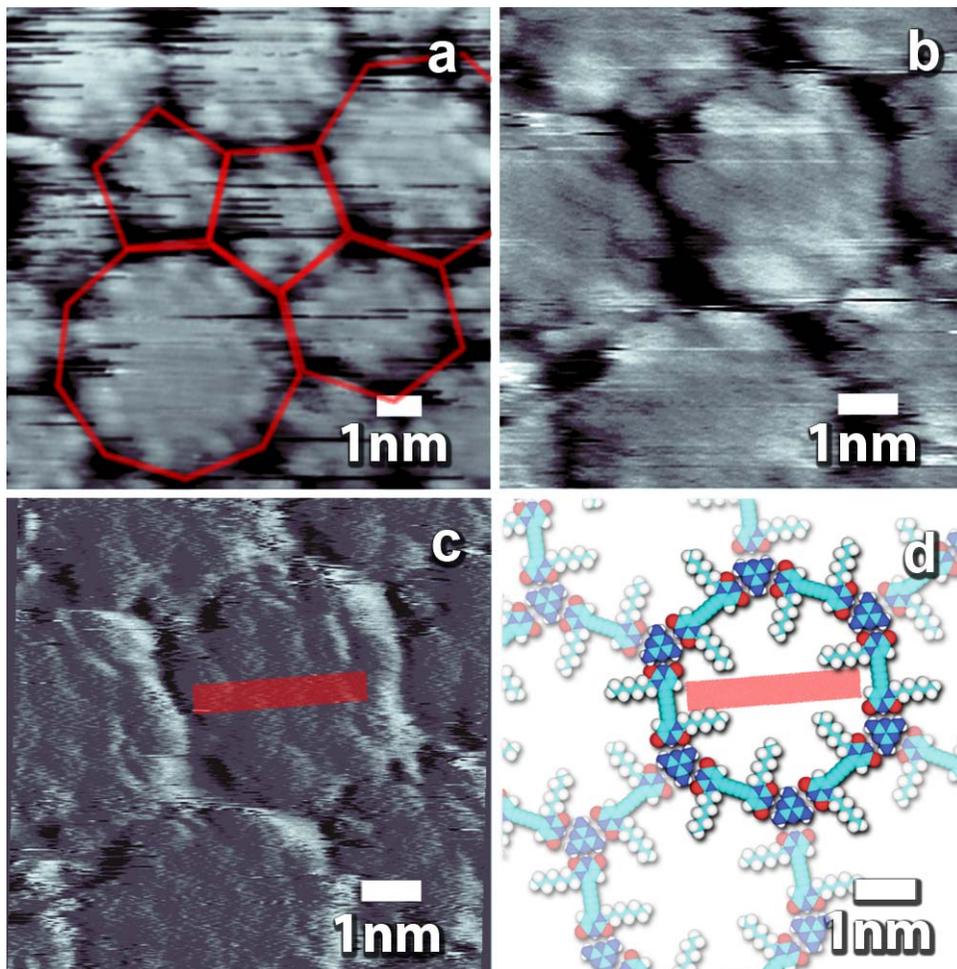
Self-assembly

Melamine and **1** in solution on graphite (HOPG)



Self-assembly

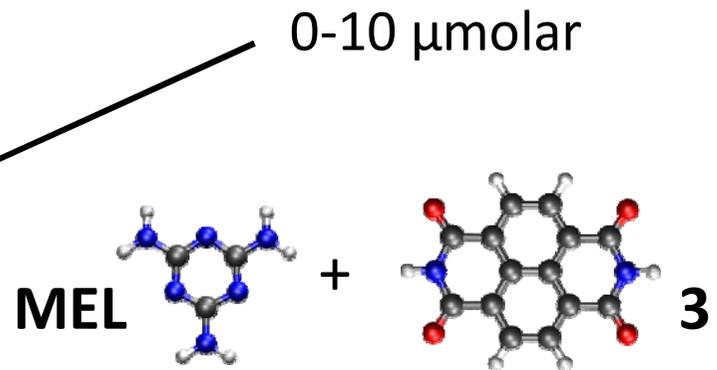
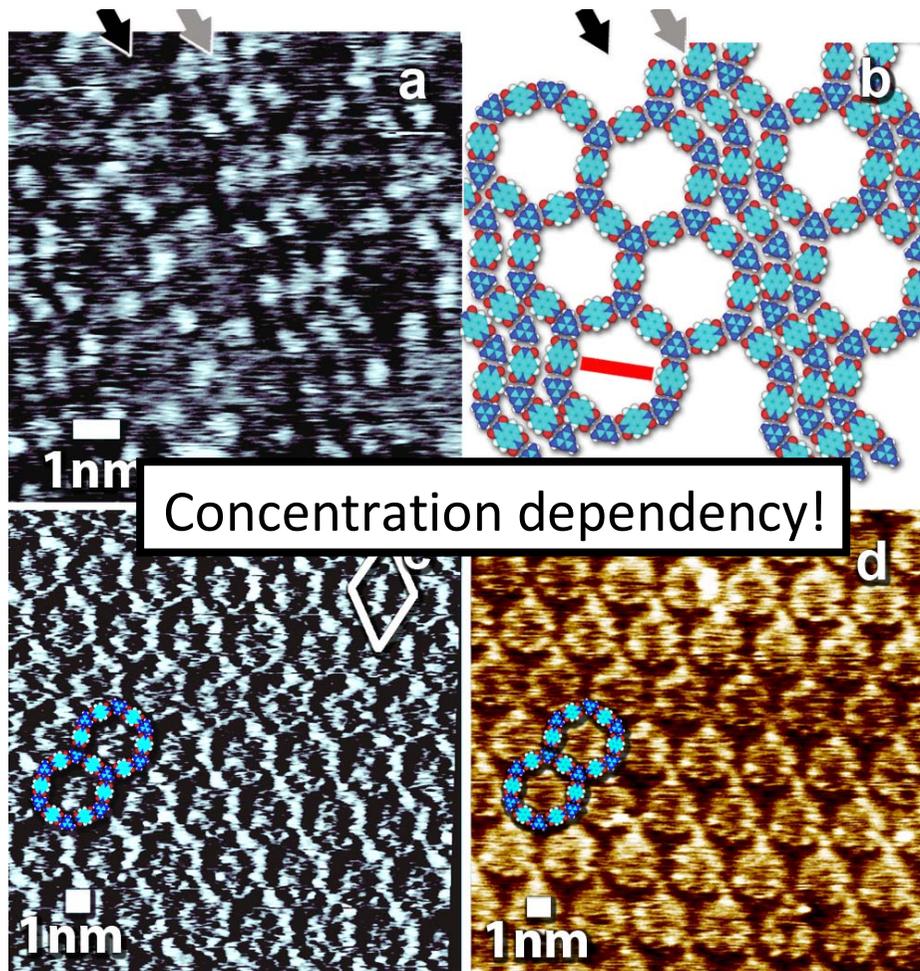
Melamine and **2** in solution on graphite (HOPG)



No ordered structure,
many kinds of
polygons observed.

Self-assembly

Melamine and **3** in solution on graphite (HOPG)

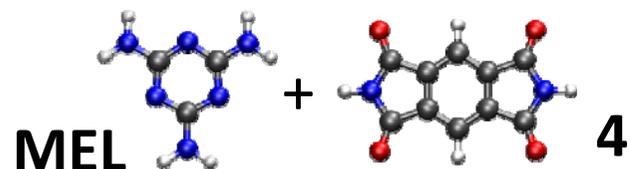
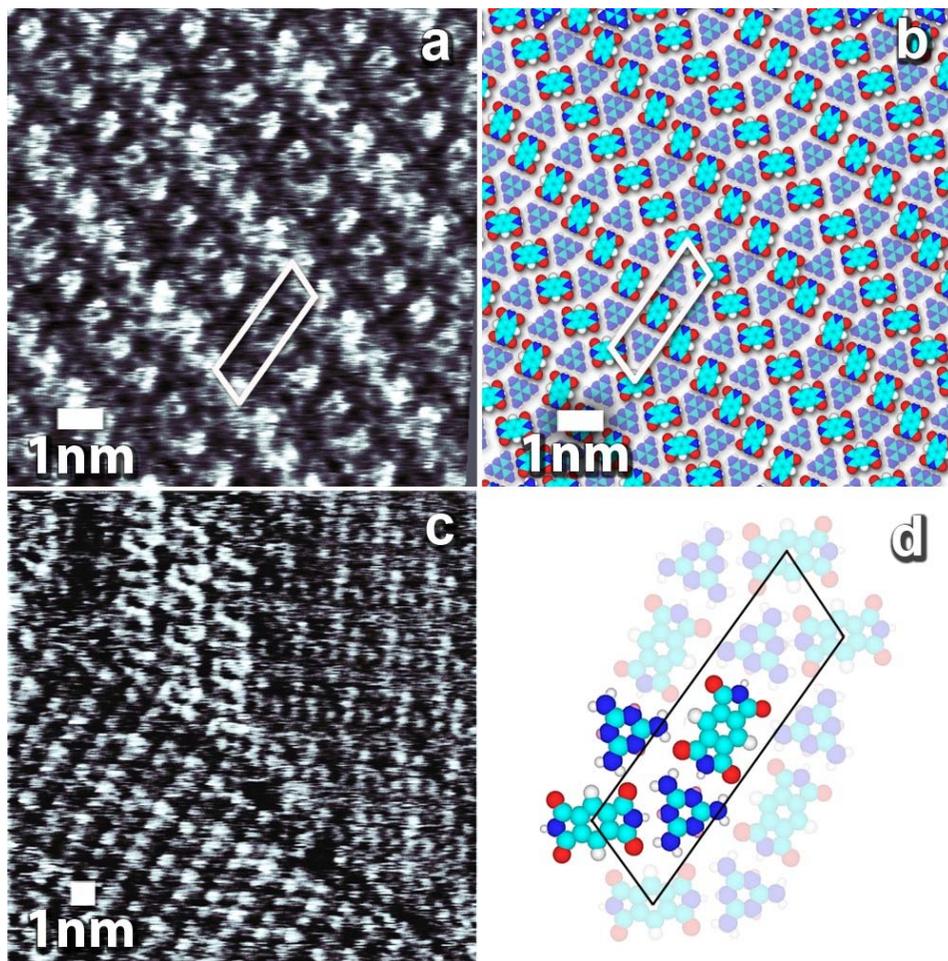


No other polygons than hexagons are observed!

10-30 μmolar MEL and 0-10 in **3**

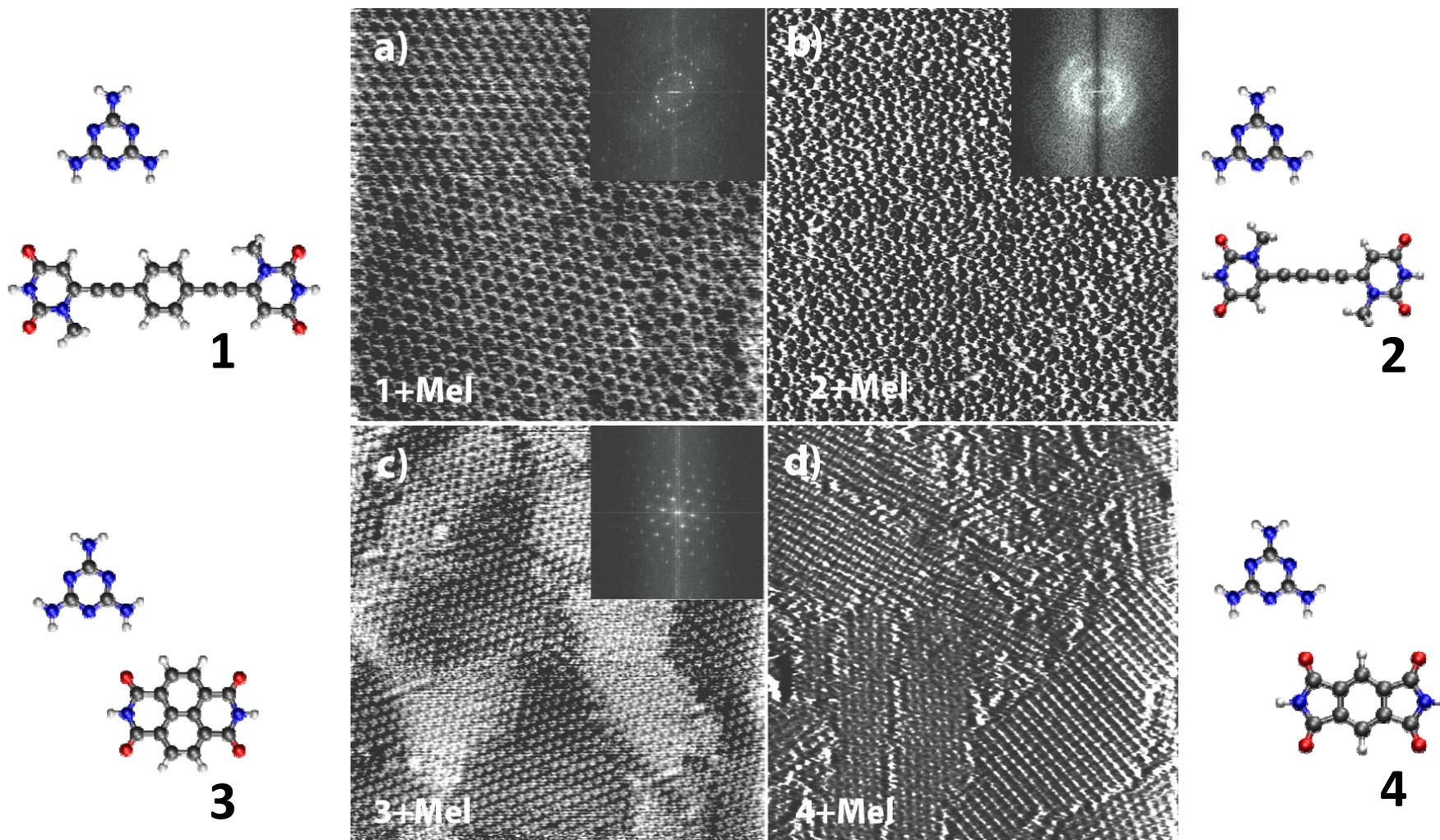
Self-assembly

Melamine and **4** in solution on graphite (HOPG)



No porous network formed. Only close-packed structures!

Long-range order?



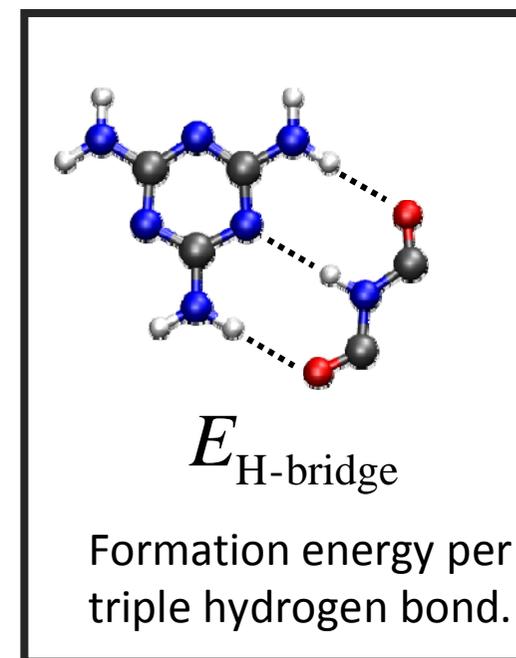
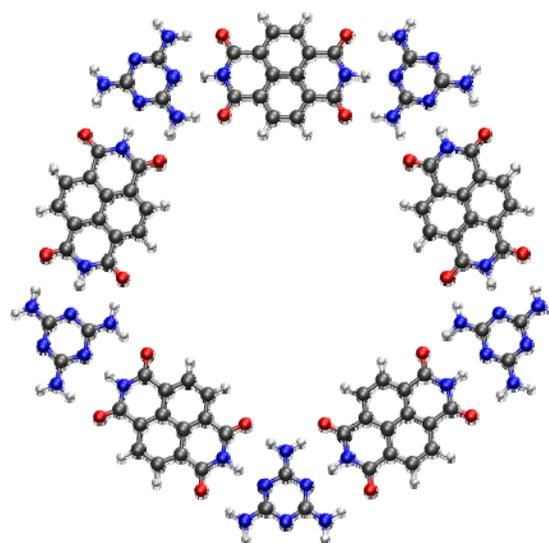
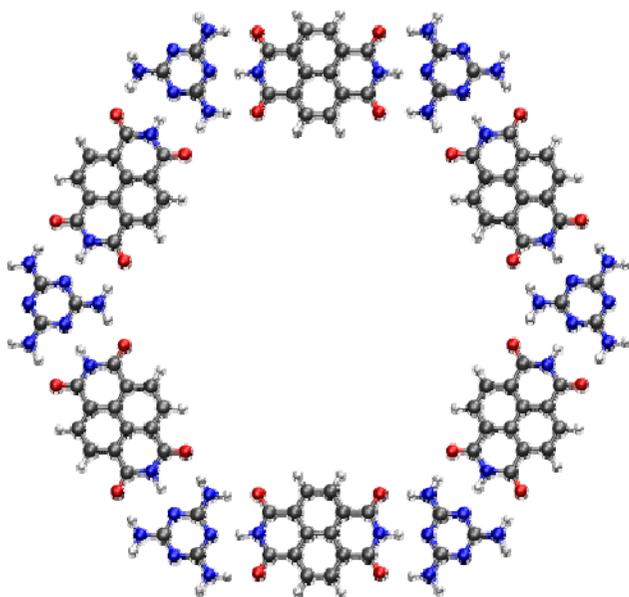
Rigidity of linkers

Isolated

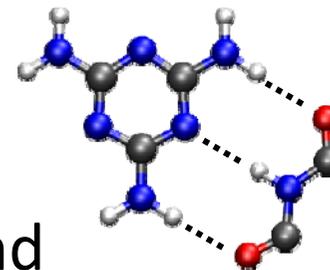
Hexagons

vs.

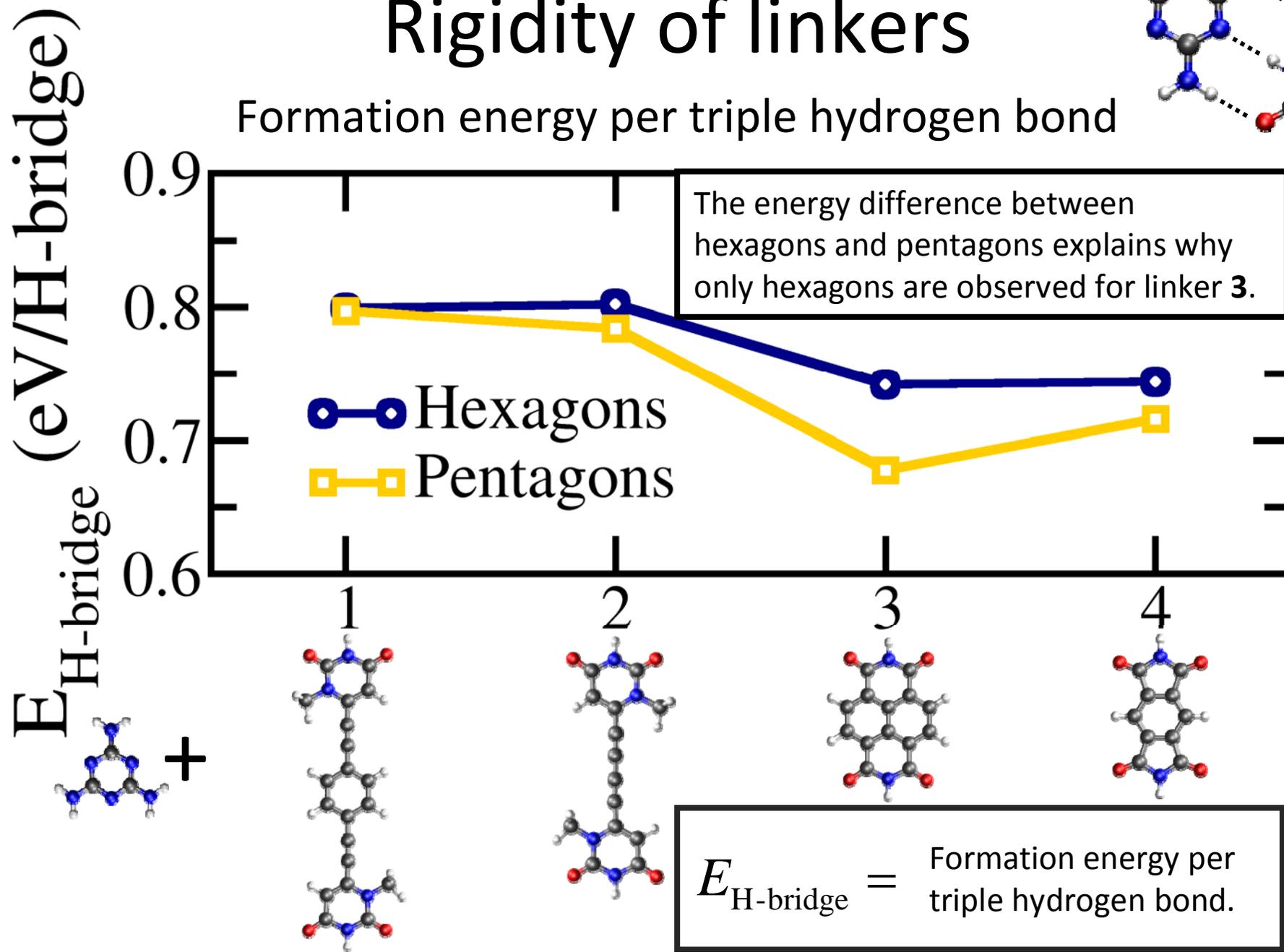
Pentagons



Rigidity of linkers



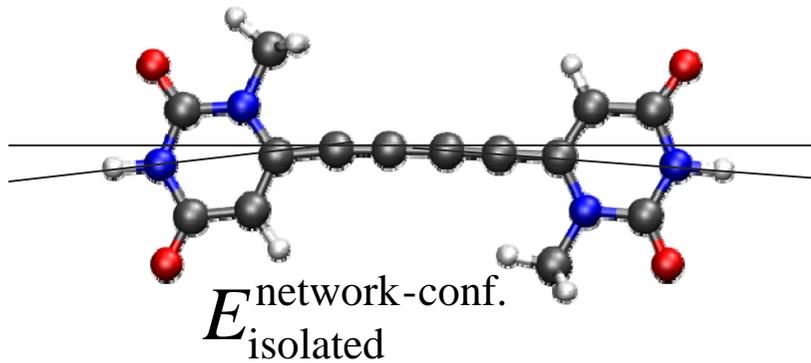
Formation energy per triple hydrogen bond



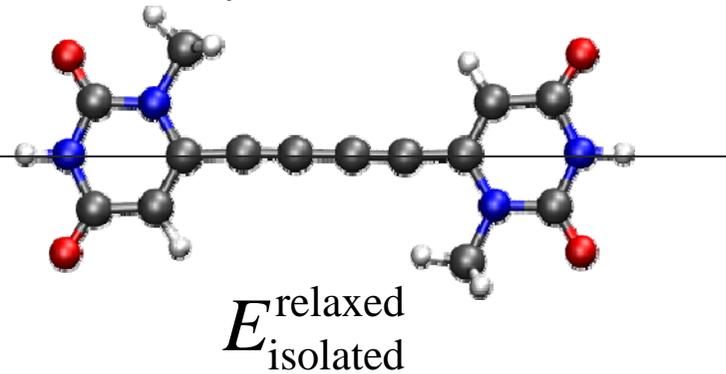
Rigidity of linkers

The deformation energy for melamine and linkers

Linker 2 from pentagonal structure



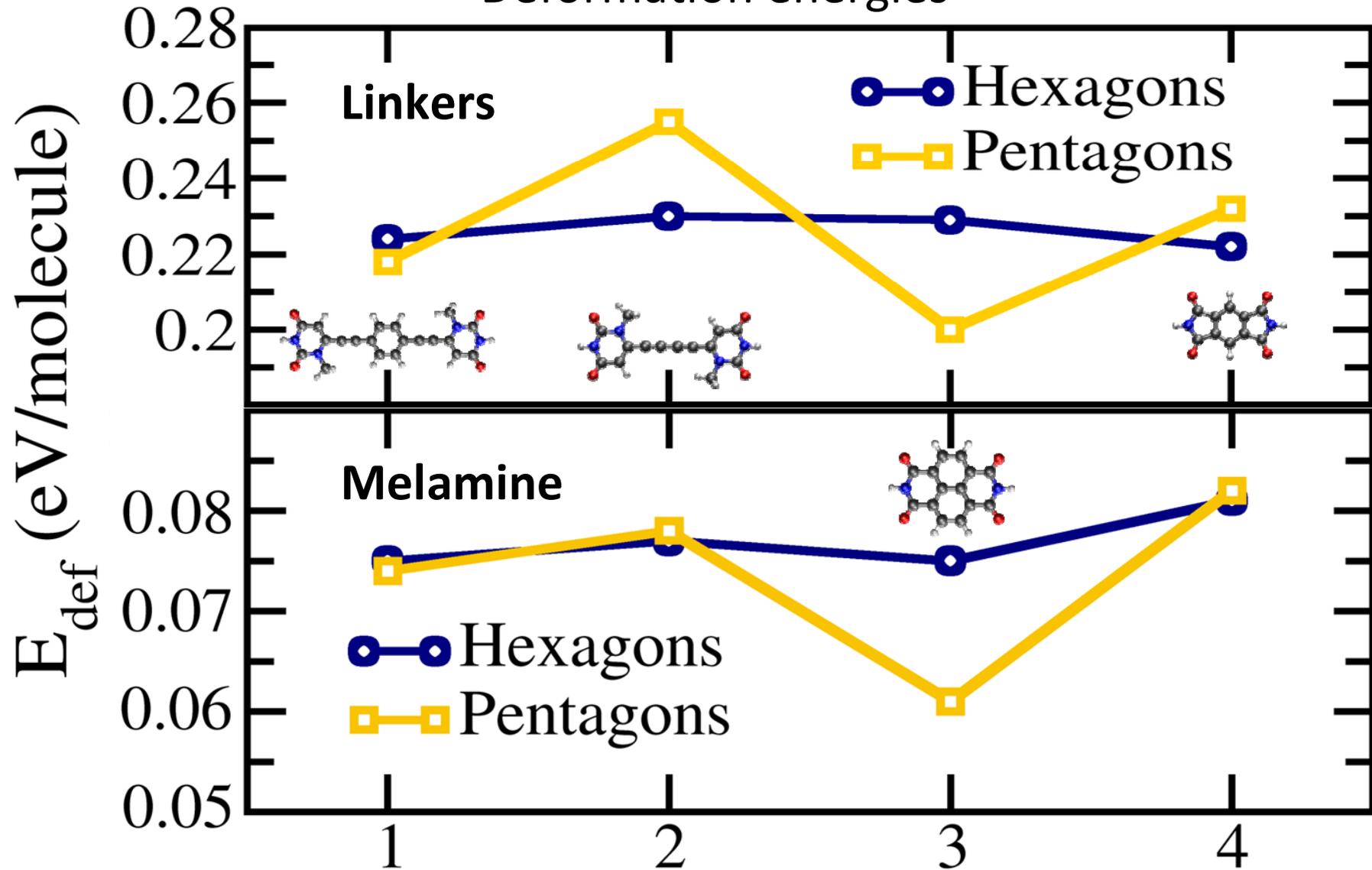
Linker 2 optimized in vacuum



$$E_{\text{def}} = E_{\text{isolated}}^{\text{network-conf.}} - E_{\text{isolated}}^{\text{relaxed}}$$

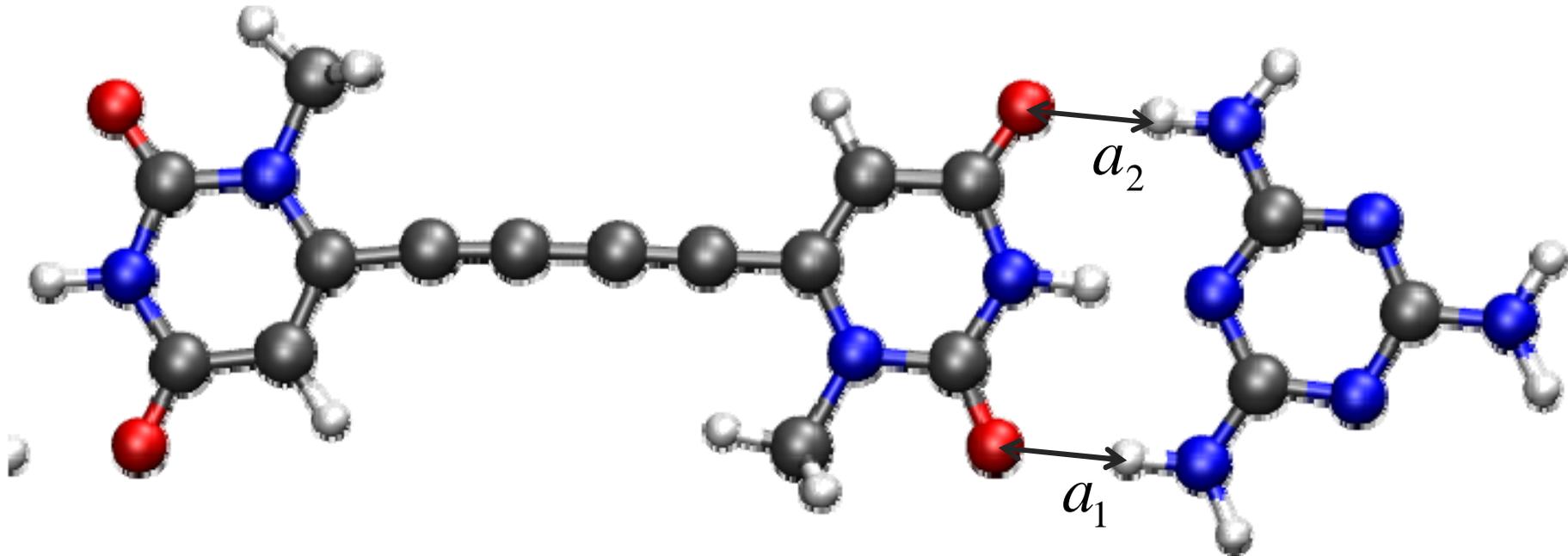
Rigidity of linkers

Deformation energies



Rigidity of linkers

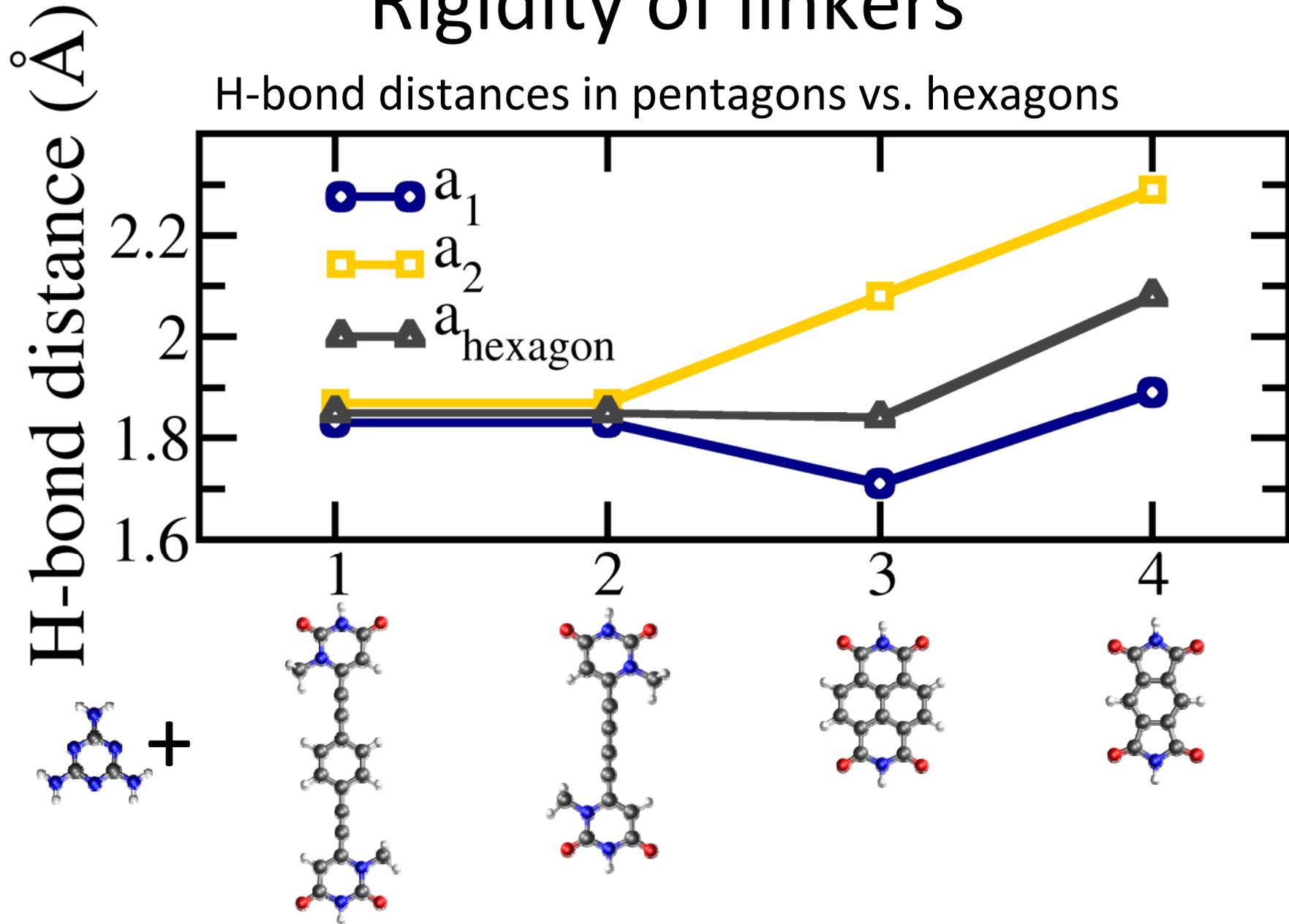
Hydrogen bond distance in pentagons vs. hexagons



For hexagons $a_1 = a_2$

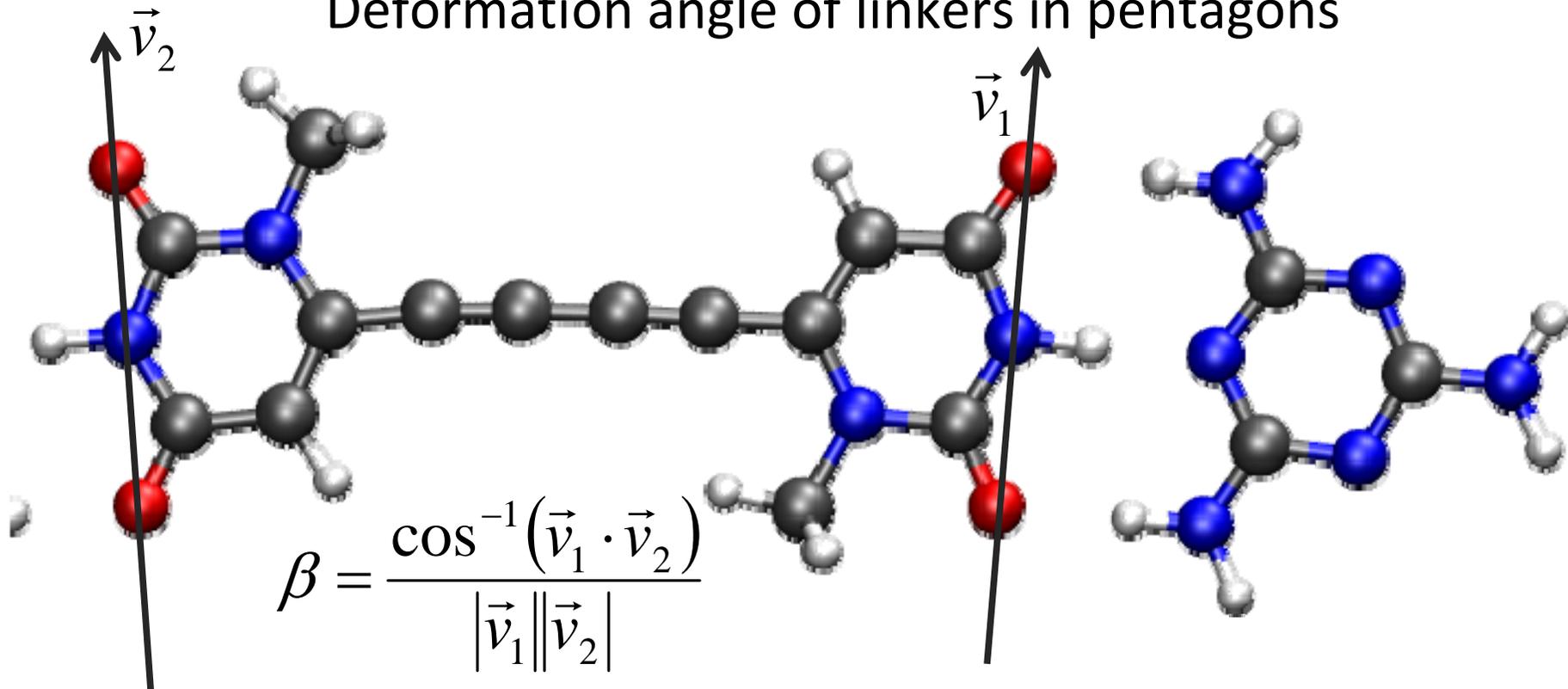
Rigidity of linkers

H-bond distances in pentagons vs. hexagons



Rigidity of linkers

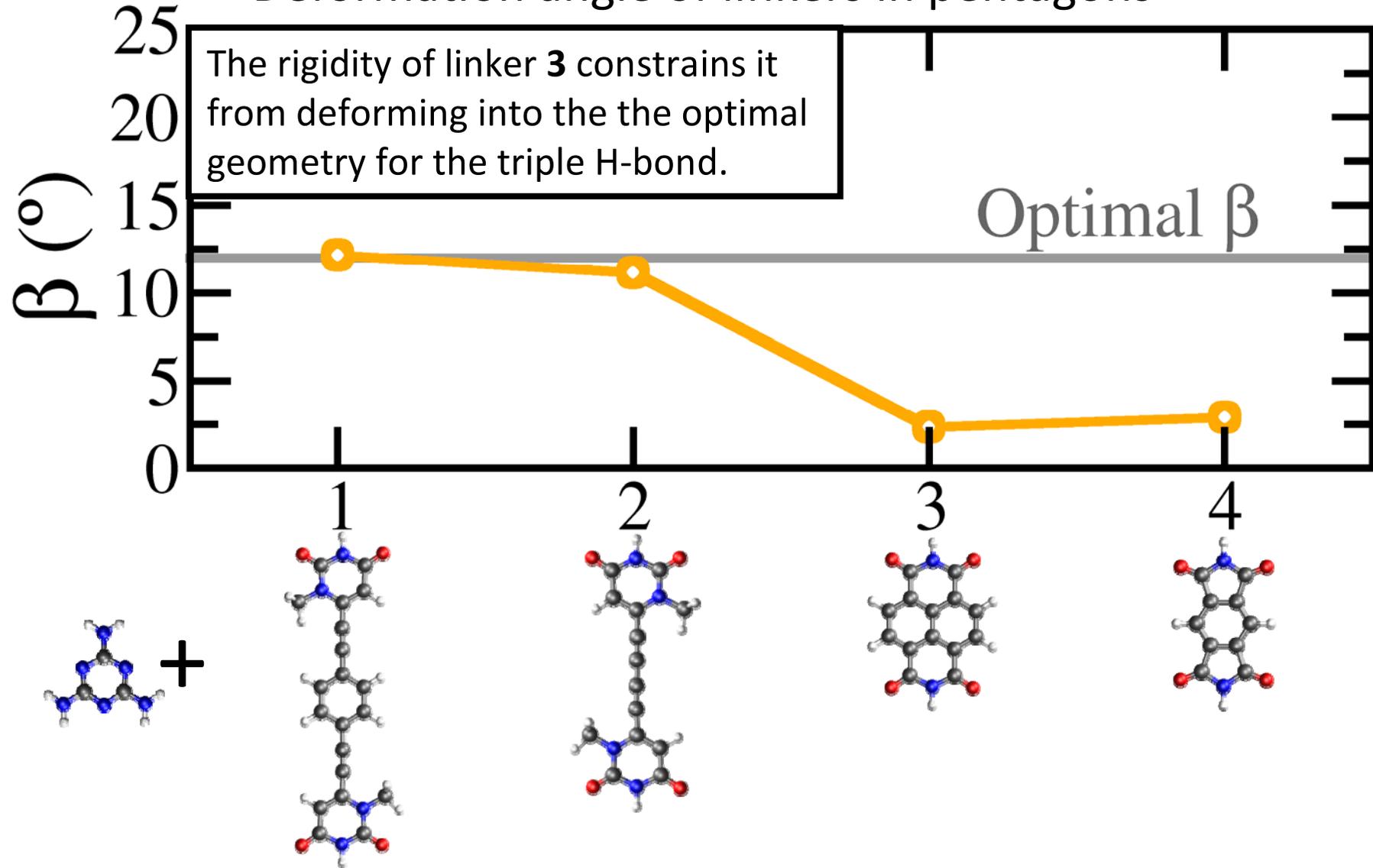
Deformation angle of linkers in pentagons



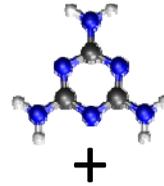
The angle spanned by \vec{v}_1 and \vec{v}_2 is defined as the deformation angle β

Rigidity of linkers

Deformation angle of linkers in pentagons

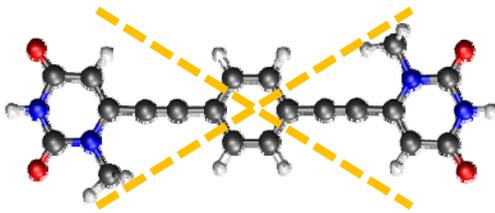


Summary

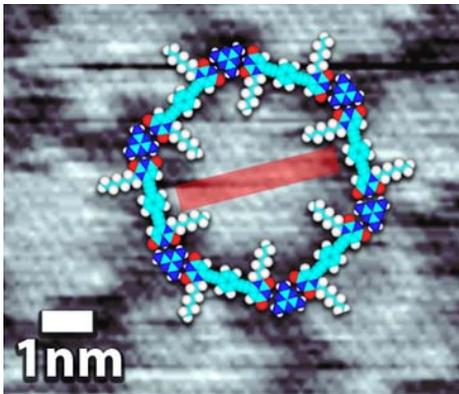


Melamine

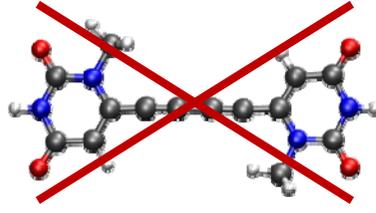
1



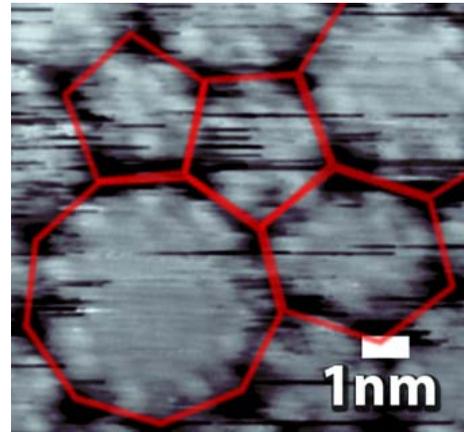
Mainly hexagons
but also other
polygons.



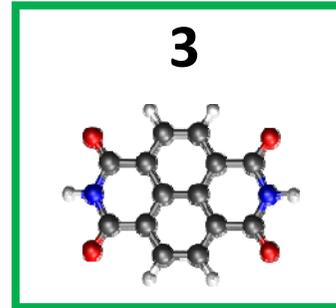
2



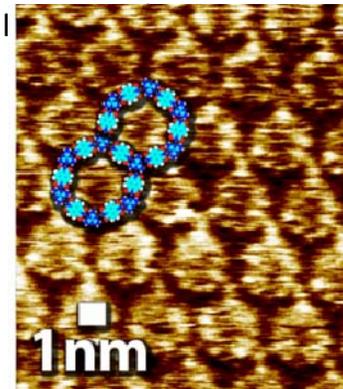
No ordered
structure.



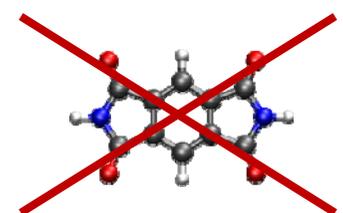
3



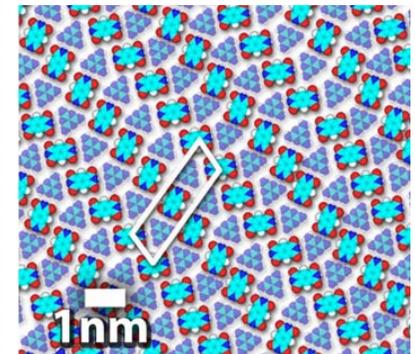
Forms long-range
ordered
hexagonal porous



4



No porous network.



Acknowledgment

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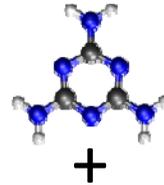
PRAIRIES network



www.prairies-network.eu

† Also at University of Namur, Belgium

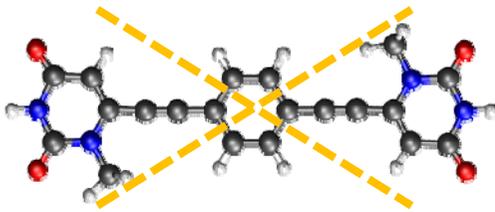
Summary



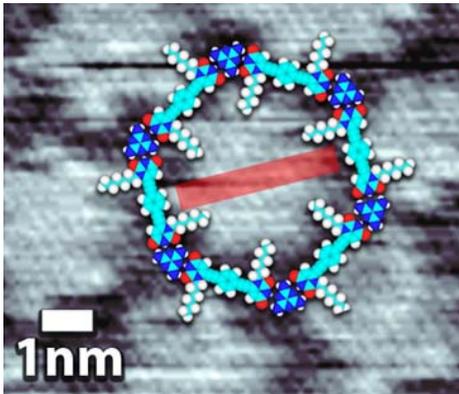
Melamine

+

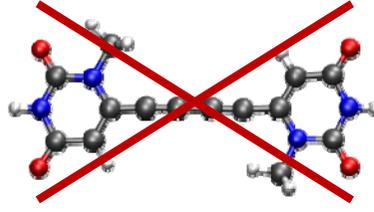
1



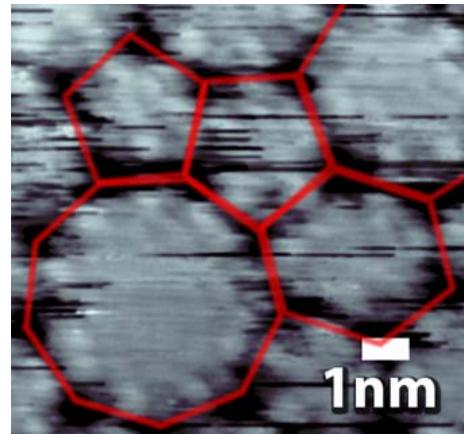
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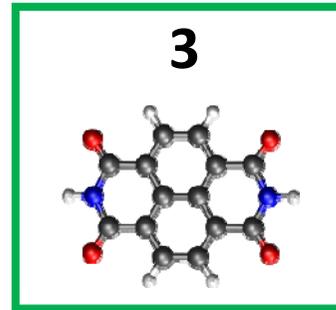
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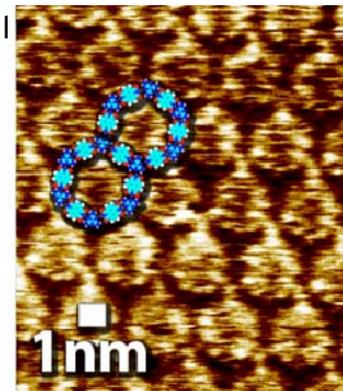
No ordered structure.



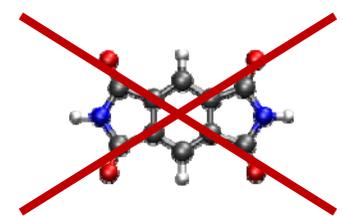
3



Forms long-range ordered hexagonal porous



4



No porous network is formed.

