2D surface confined nanoporous molecular networks at the liquid-solid interface: a scanning tunneling microscopy study

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Content

- Introduction
- Two strategies toward formation of flexible porous networks
  - Concentration control
  - Guest induced transformation
- Conclusion

2D organic nanoporous networks

Ordered structures with cavities formed by organic molecules on top of a solid substrate.

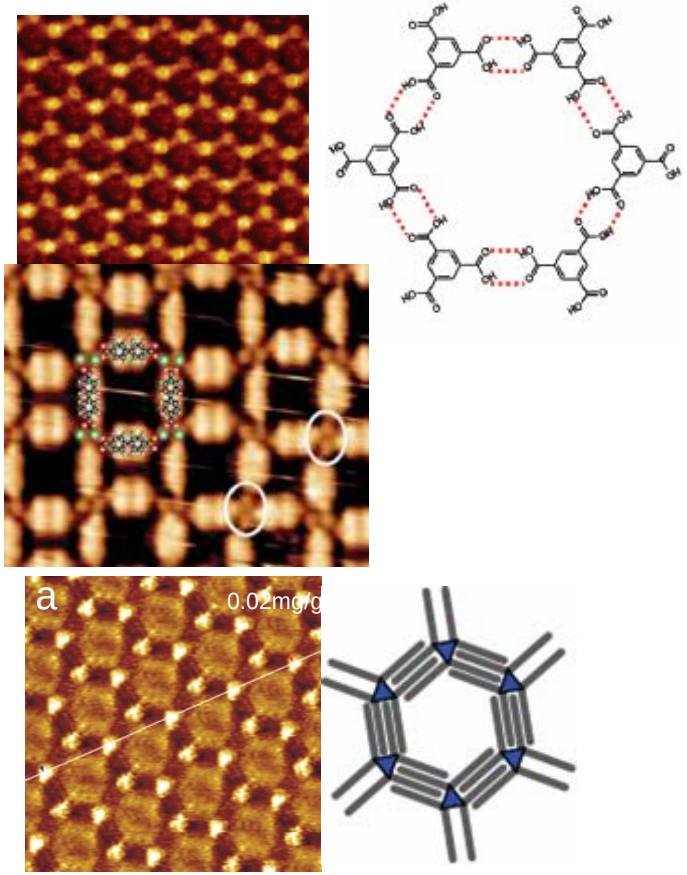
2D analogues of Zeolite and Metal-organic frameworks

Interactions involved

Hydrogen bonding

Metal-organic coordination

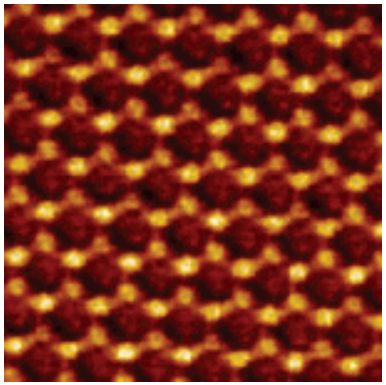
Van der Waals forces

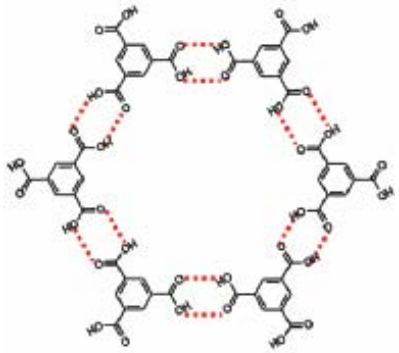


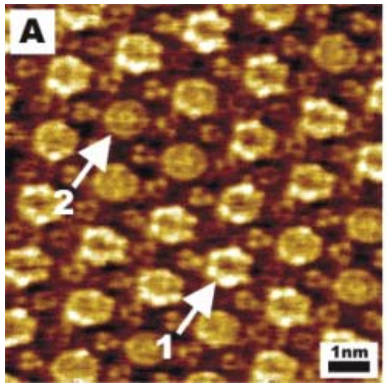
Application of the 2D nanoporous networks

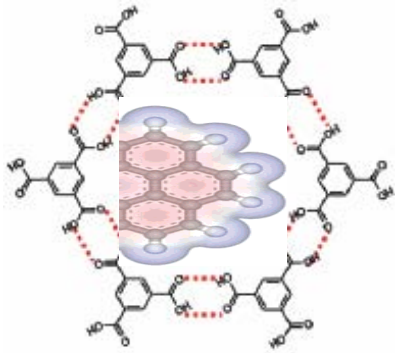
Template

Assembling of other organic molecules in a predefined manner

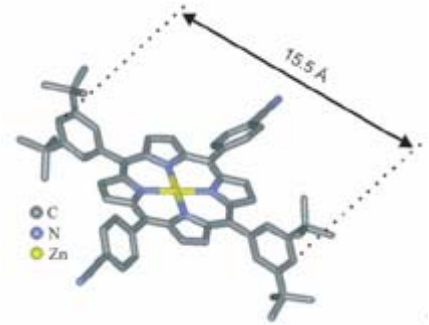


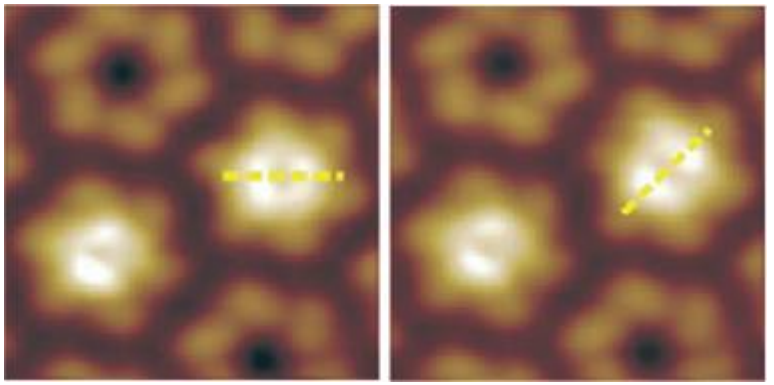






Molecular device





Langmuir, Vol. 20, 2004, 9403.

Angew. Chem. Int. Ed. **2007**, *46*, 4089.

Challenges

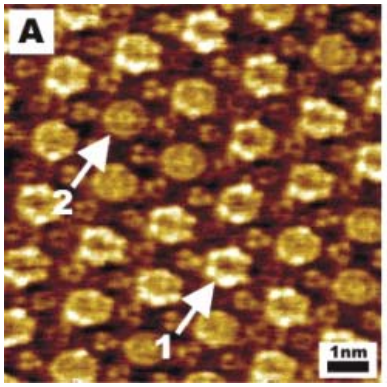
Adjusting the pore size

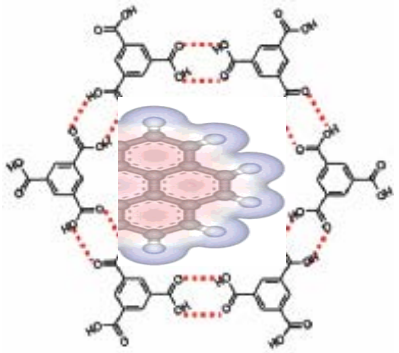
Size available: from < 1 nm to 5 nm

Adjust the pore size sequentially.
Larger size possible?

Hosting molecular clusters

——beyond the state of art

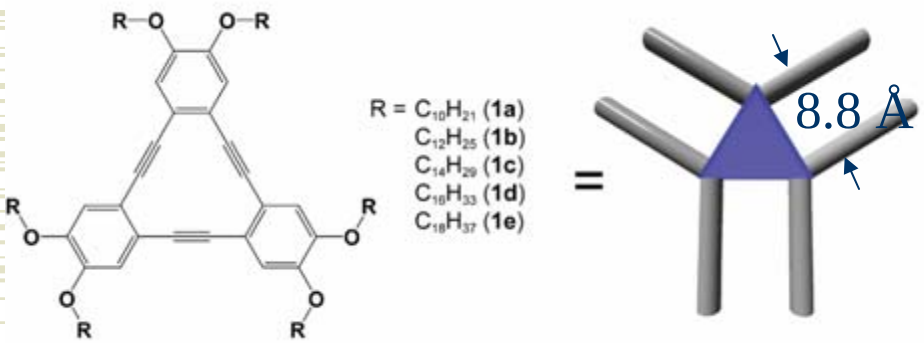




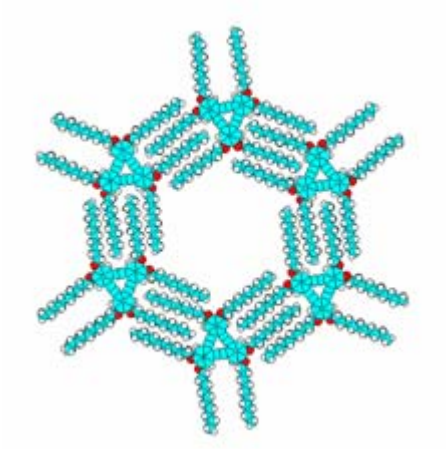
nanovessels for chemical reaction

Langmuir, Vol. 20, 2004, 9403.

Flexible porous network based on alkyl chain interdigitations



Dehydrobenzo[12]annulene Derivatives
DBA-OC_n



Honeycomb structure

Tahara K. et al. J. Am. Chem. Soc. **2006**, *16613*

Advantage:

adjustable with high precision, ~ 2.5 Å

Parameters of the honeycomb structure formed by DBA-OCn

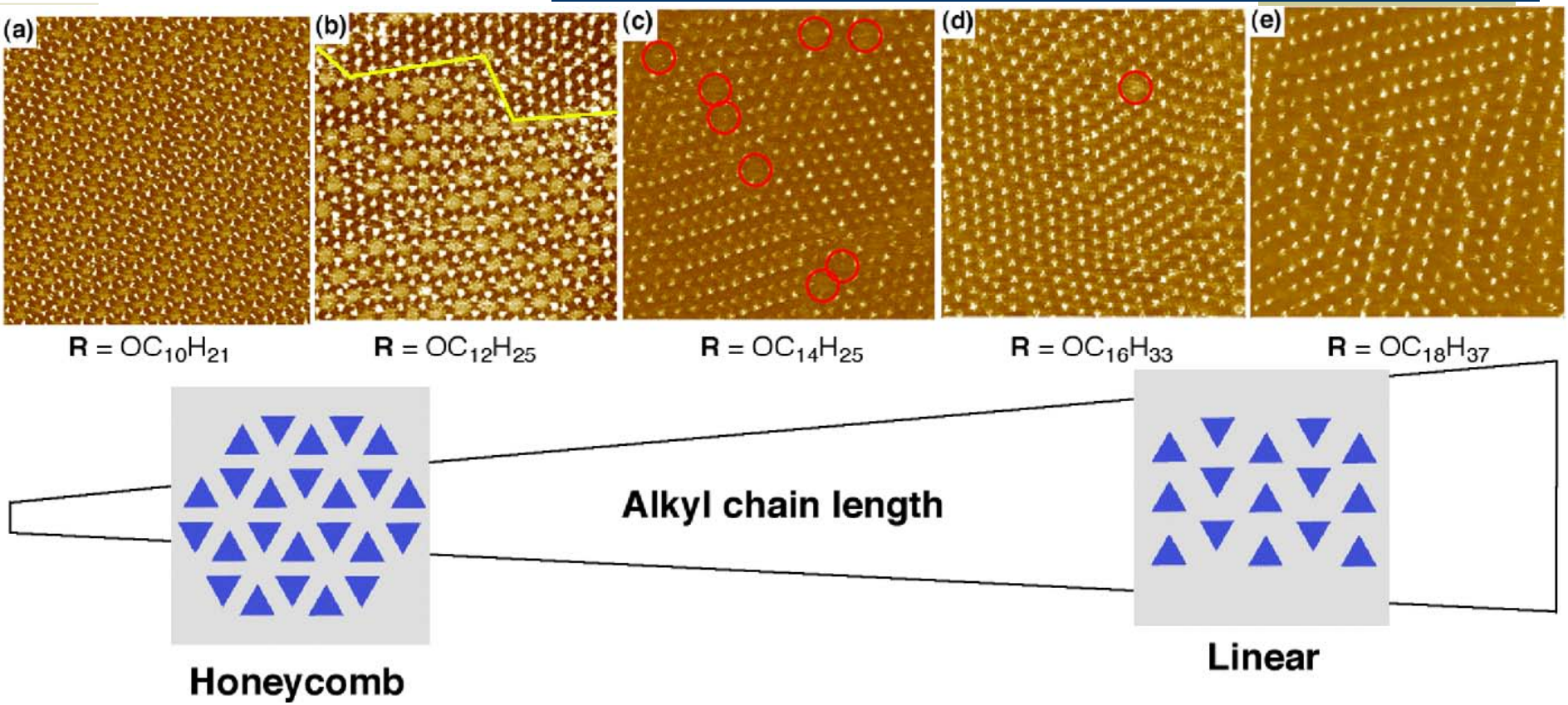
	DBA-OC10	DBA-OC12	DBA-OC14	DBA-OC16	DBA-OC18	DBA-OC20
Repeating period (honeycomb)/nm	4.1	4.6	5.0	5.5	5.9	6.3
Size of the pore Corner-to-Corner	**2.9**	**3.5**	**3.9**	**4.5**	**5.0**	**5.4**
Area of unit cell /nm^2	14.6	17.9	21.7	25.7	30.1	34.4
Percentage of pore /%	37	42	46	50	53	56

So in principle we can get nanopores with diameter ranging from 2.9 nm up to 5.4 nm using these DBAs as building blocks.

Effects of alkyl chain lengths (MS interaction)

In TCB, **concentration 1 mg/ml**

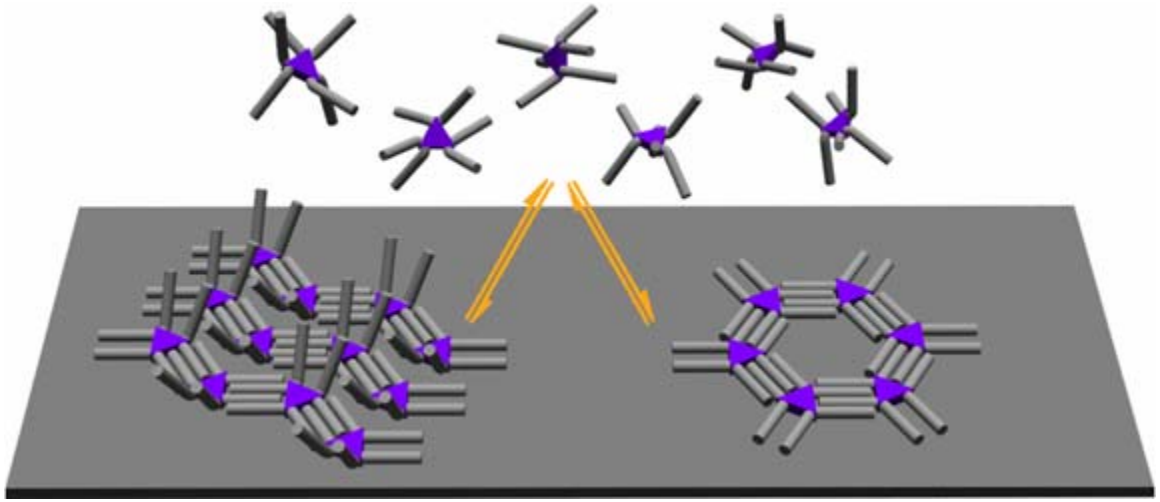
OC10 **OC12** **OC14** **OC16** **OC18**



Two strategies

- Adjusting the concentration
- Guest induced transformation

Concentration dependent formation



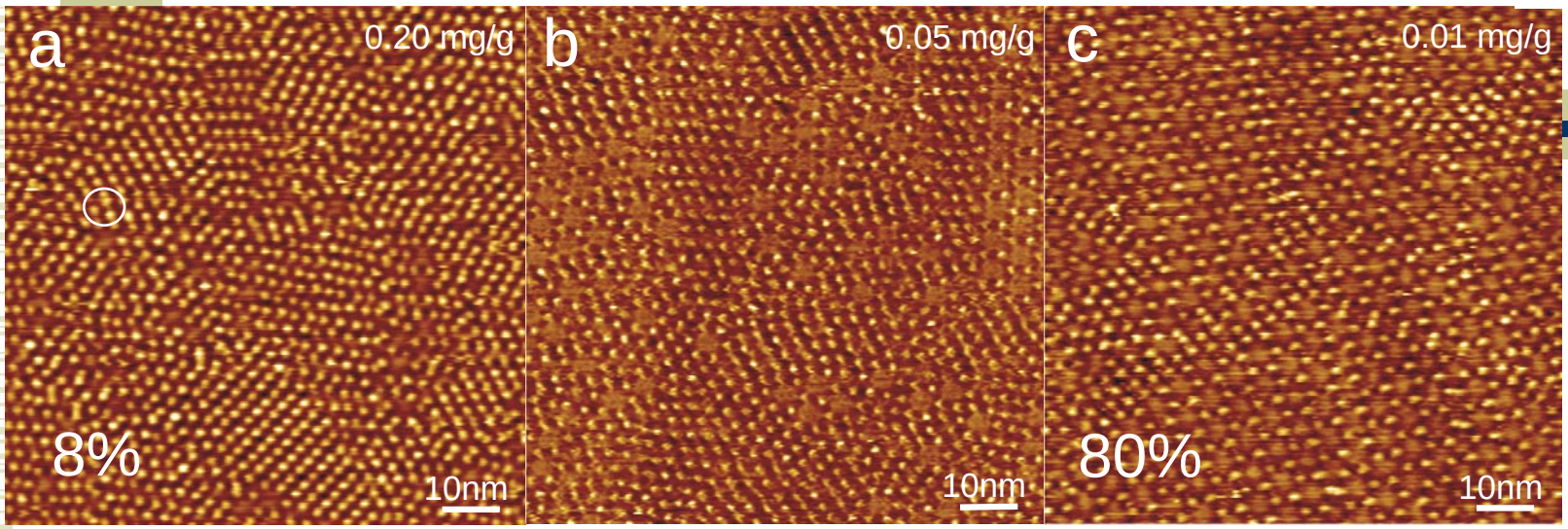
The concentration of the solution determines the number of molecules on the surface.

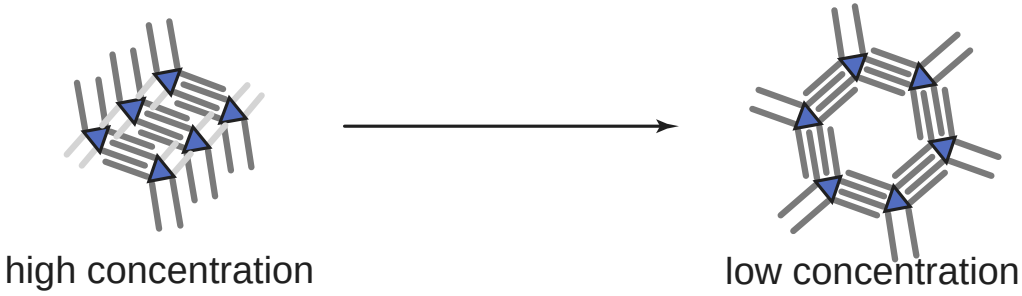
Angew. Chem. Int. Ed. 2008, 47, 2964 –2968

http://go.to/funpic

DBA-OC16

1.1×10^{-4} M 2.1×10^{-5} M 5.7×10^{-6} M

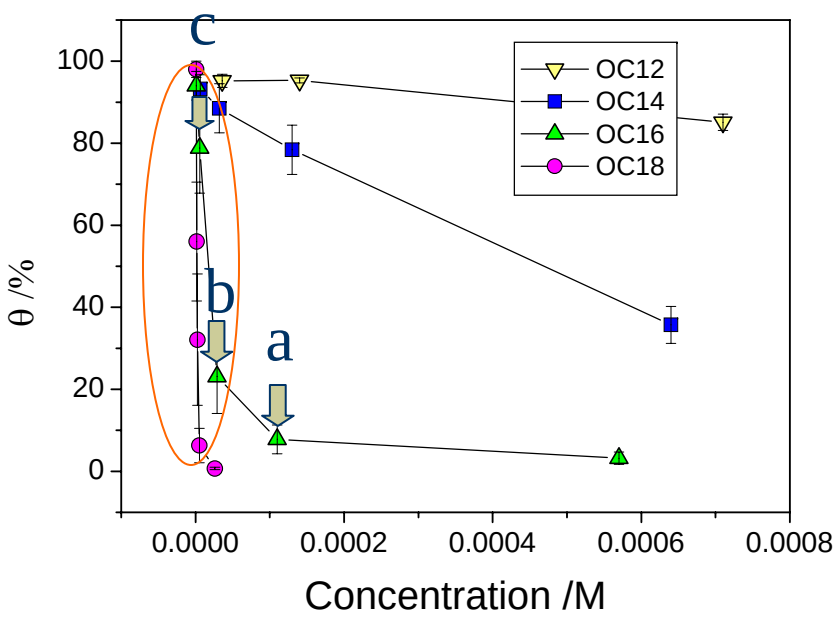


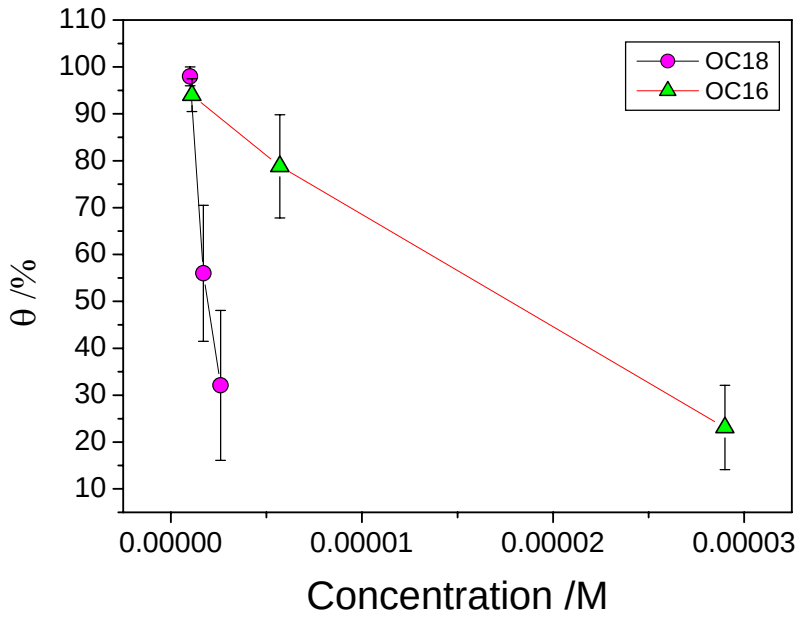


A series of STM images obtained with different concentration of DBA-OC16.

•General phenomena

•In a certain concentration range the surface coverage of porous structures show a linear dependence on concentration



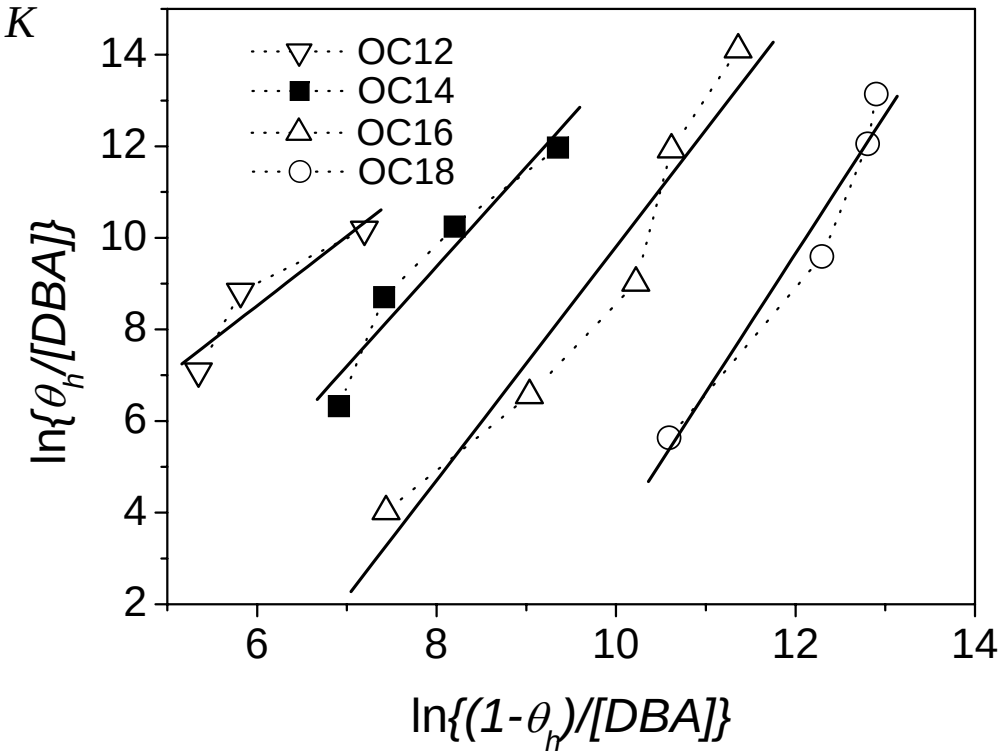


A thermodynaomic model

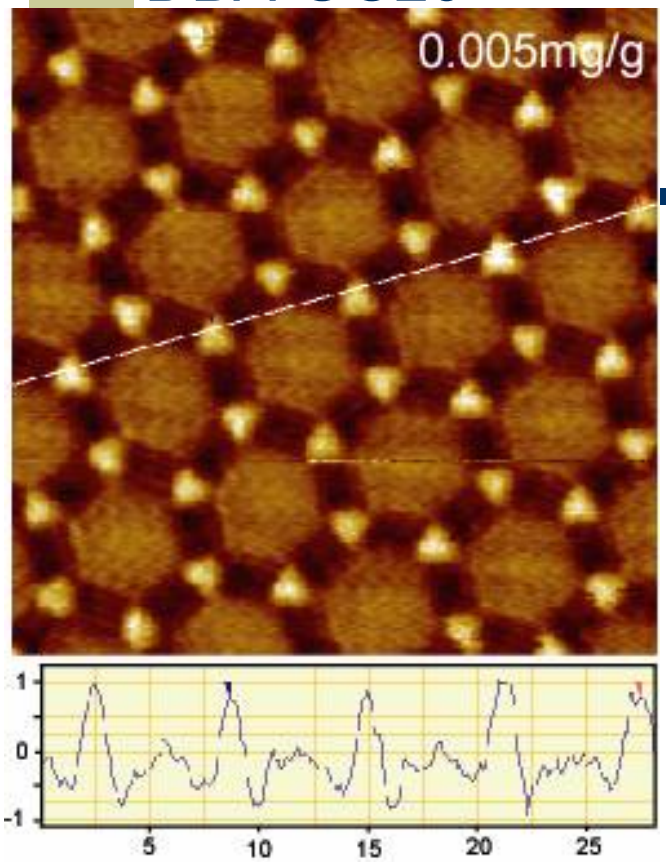
At equilibrium

$\overline{\mu}_l = \overline{\mu}_{sol}$ and $\overline{\mu}_h = \overline{\mu}_{sol}$

$$\ln\left(\frac{\theta_h}{[DBA]}\right) = m\ln\left(\frac{1-\theta_h}{[DBA]}\right) + \ln K$$

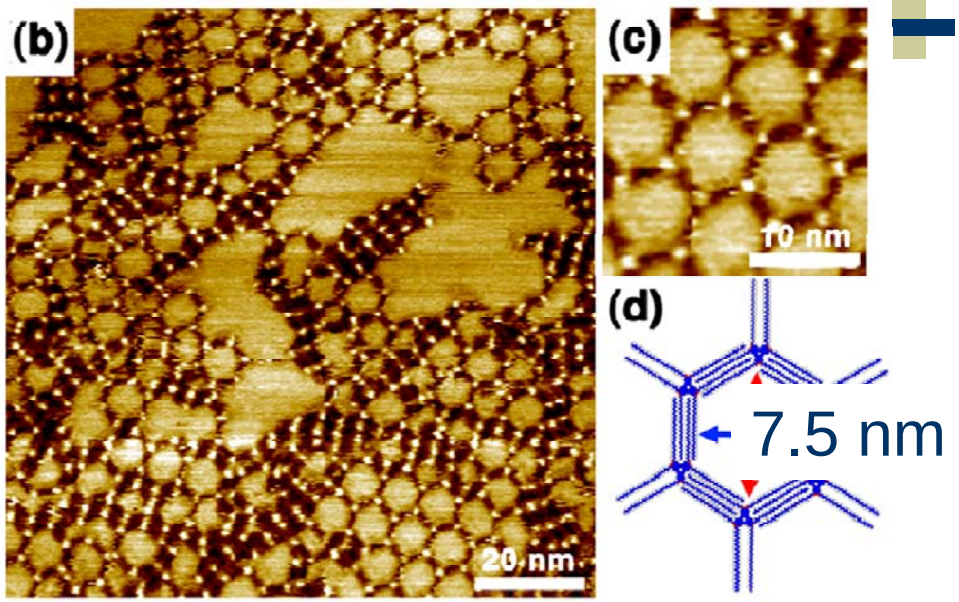


DBA-OC20



2.4×10^{-6} M

DBA-OC30

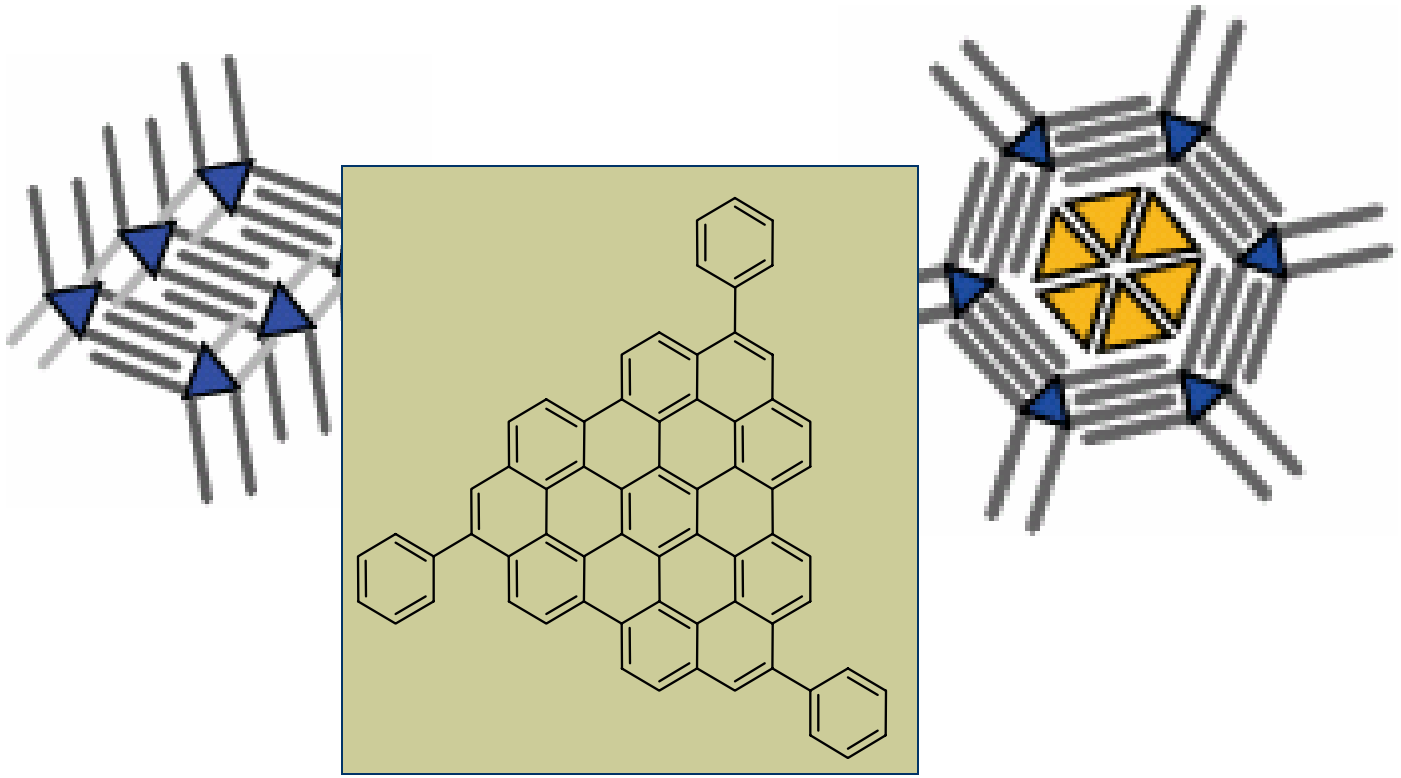


5.0×10^{-6} mol/L

Nanopores with diameter ranging from 2.9 nm up to 7.5 nm could be formed.

The pore diameter could be tuned with precision of 0.25 nm.

Guest induced transformation



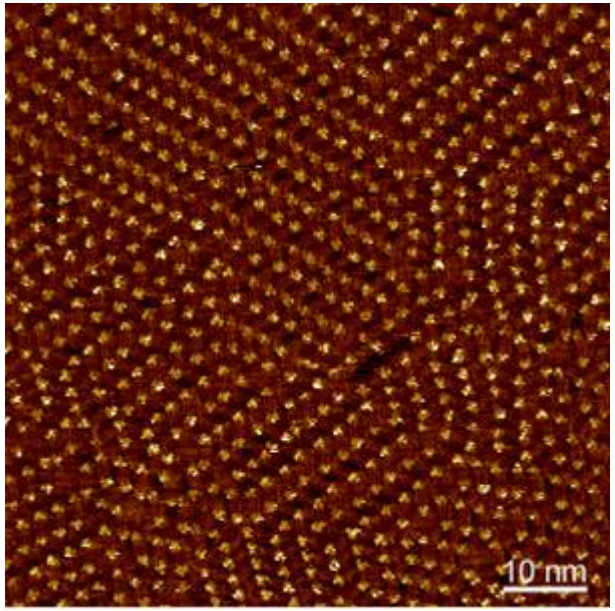
J. Am. Chem. Soc. 2008, in press.

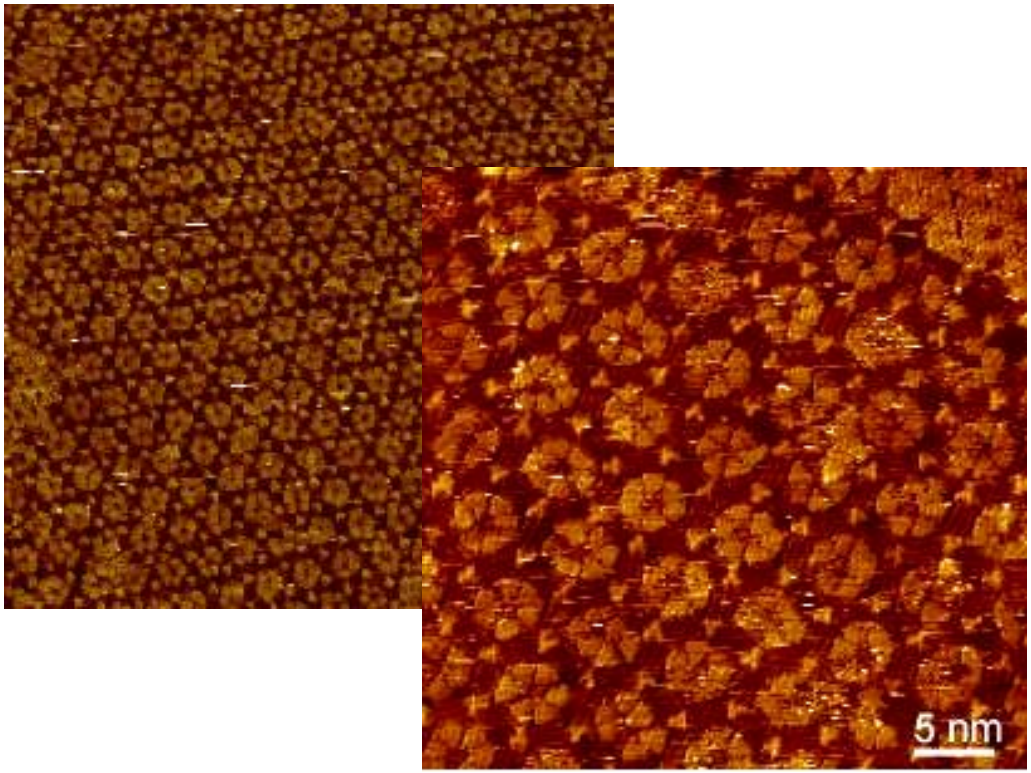
Organic Porous Frameworks in 2D: tunable in size? Yes, but..

Without guest

Concentration of DBAs: 0.05 mg/ml

With guest

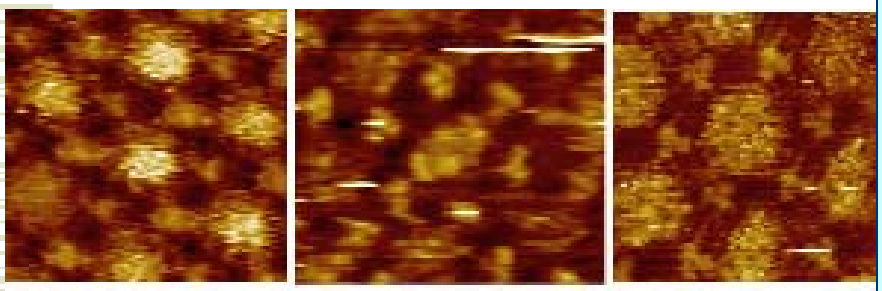


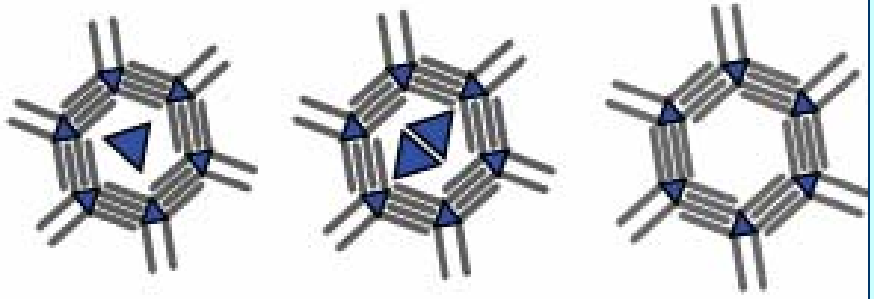


Tunable size of the cavities

One to six nanographenes could be hosted.

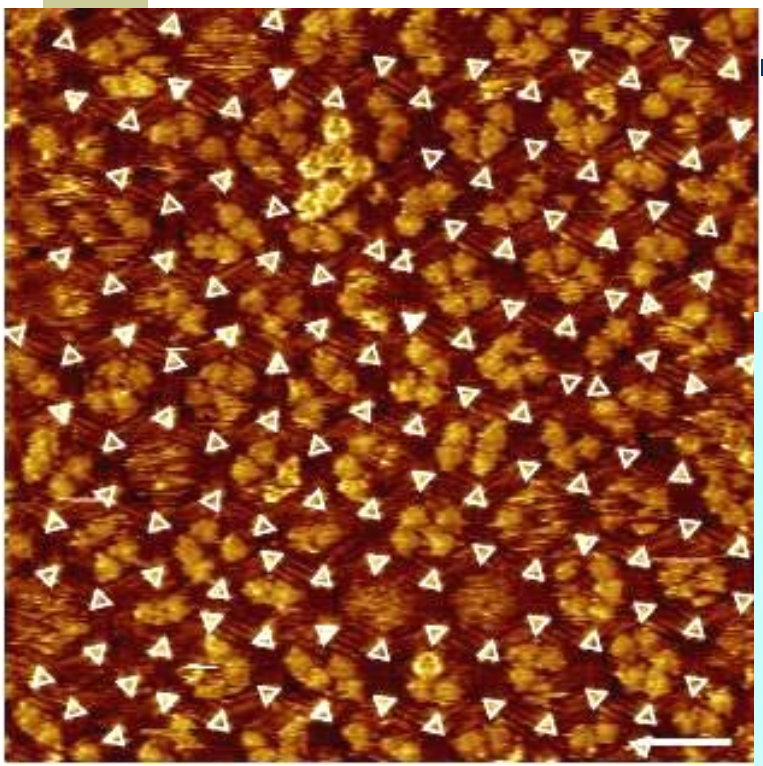
OC10 OC12 OC14 OC16 OC18 OC20

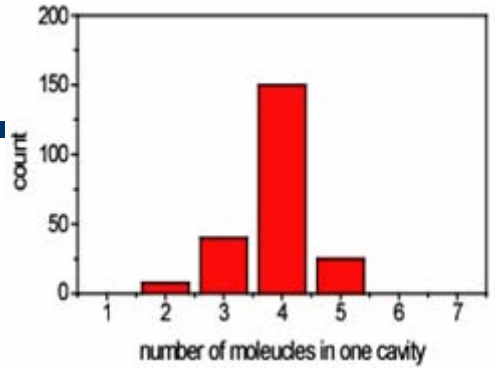


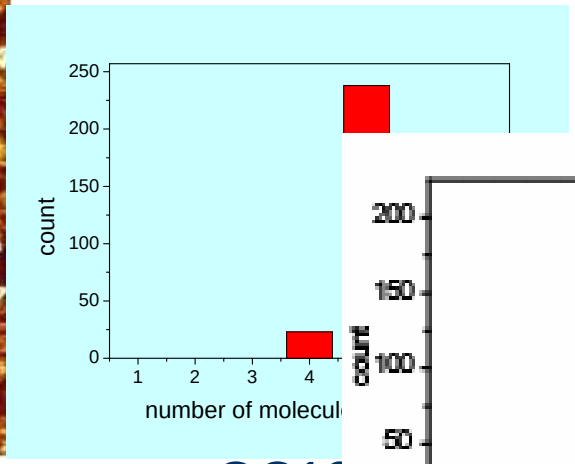


Allows us to adjust the number of molecules, the geometry in the cluster.

DBA-OC16, different guest clusters, dimers to pentamers

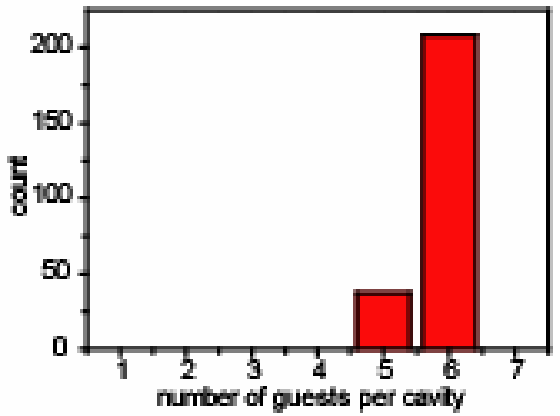






OC18

OC20



Flexibility.

The host matrix changes its structure in order to accommodate the adsorption of the guest clusters.

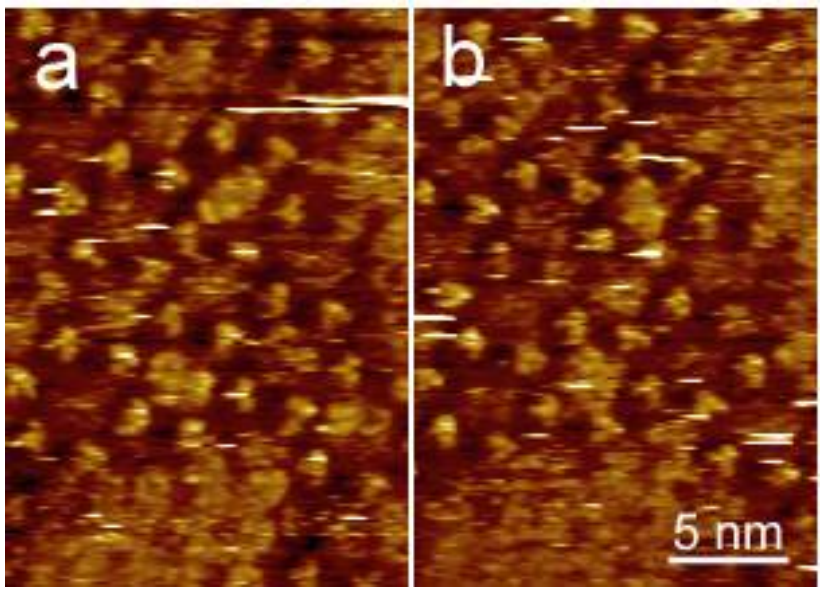
Dynamics within the host-guest matrix

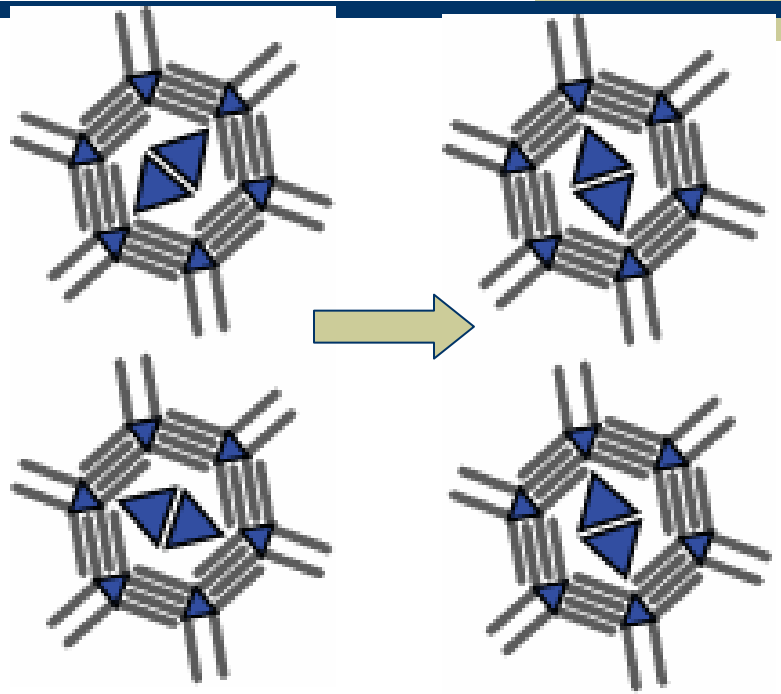
Dynamics of the guest inside the cavity

Migration of the guest between cavities

Dynamics of the host molecules

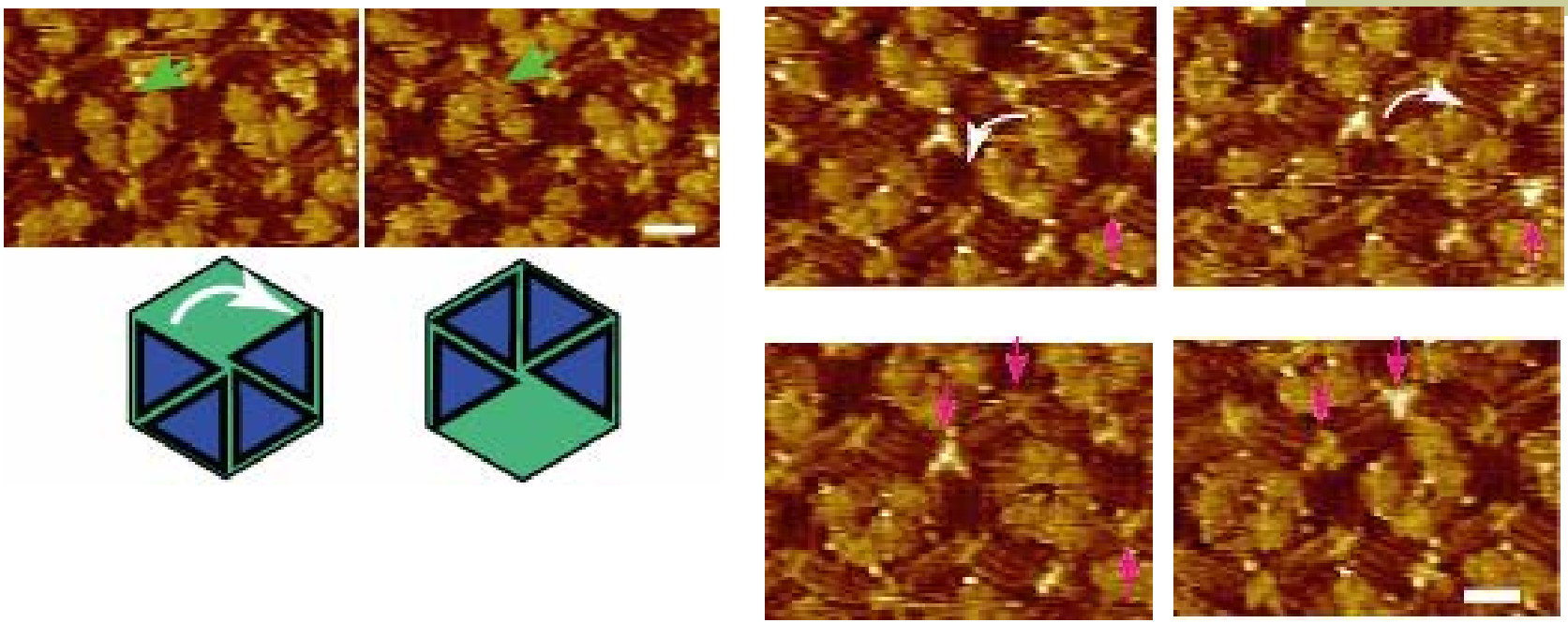
Rotation of the nanographene dimers inside the cavity of DBA-OC12





Note the length of the dimer is larger than the diameter of the cavity.
3.8 nm vs 3.5 nm

Rotation of the clusters inside the cavity



These observations indicate the rotation angles are multiples of 60°.

The rotation of the guest cluster is a cooperative movement of the host-guest architecture.

Conclusion

2D nanoporous networks could be form with two different strategies: concentration control and guest induced transformation.

Tunable size and period, flexible

Beyond the art

Hosting molecular clusters, paved the way toward to use such nanoporous host matrices as nanoreactors

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