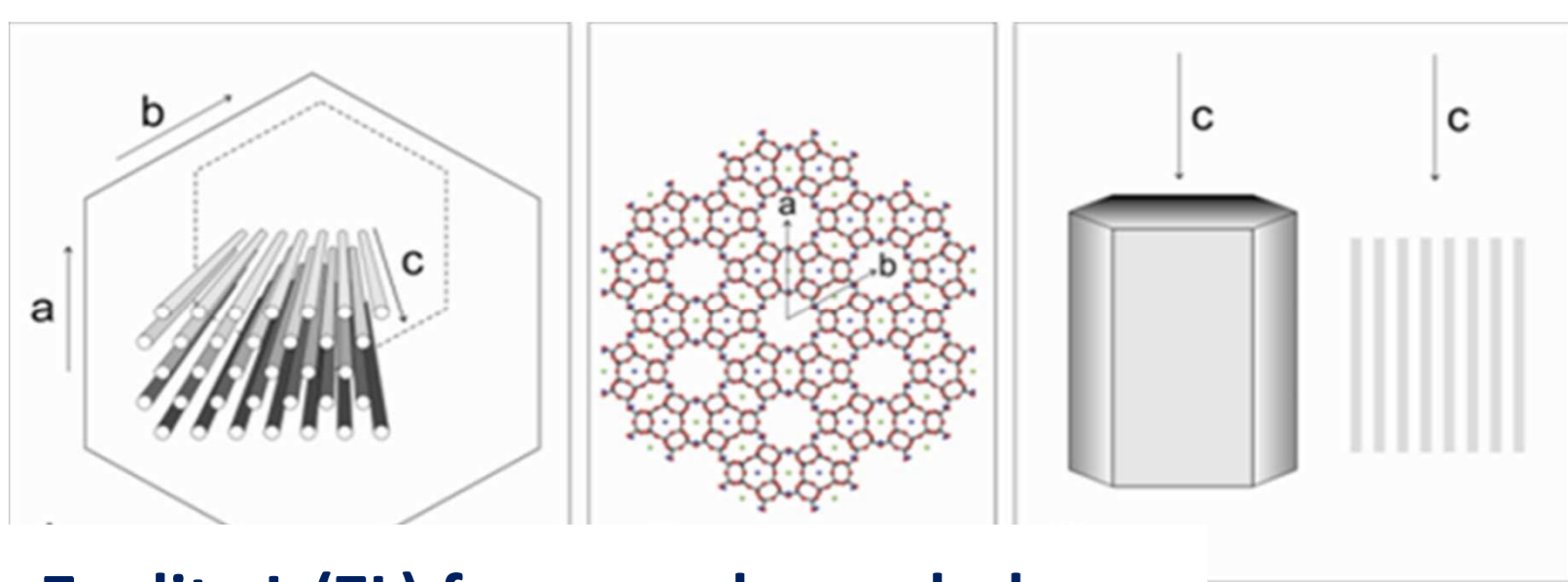


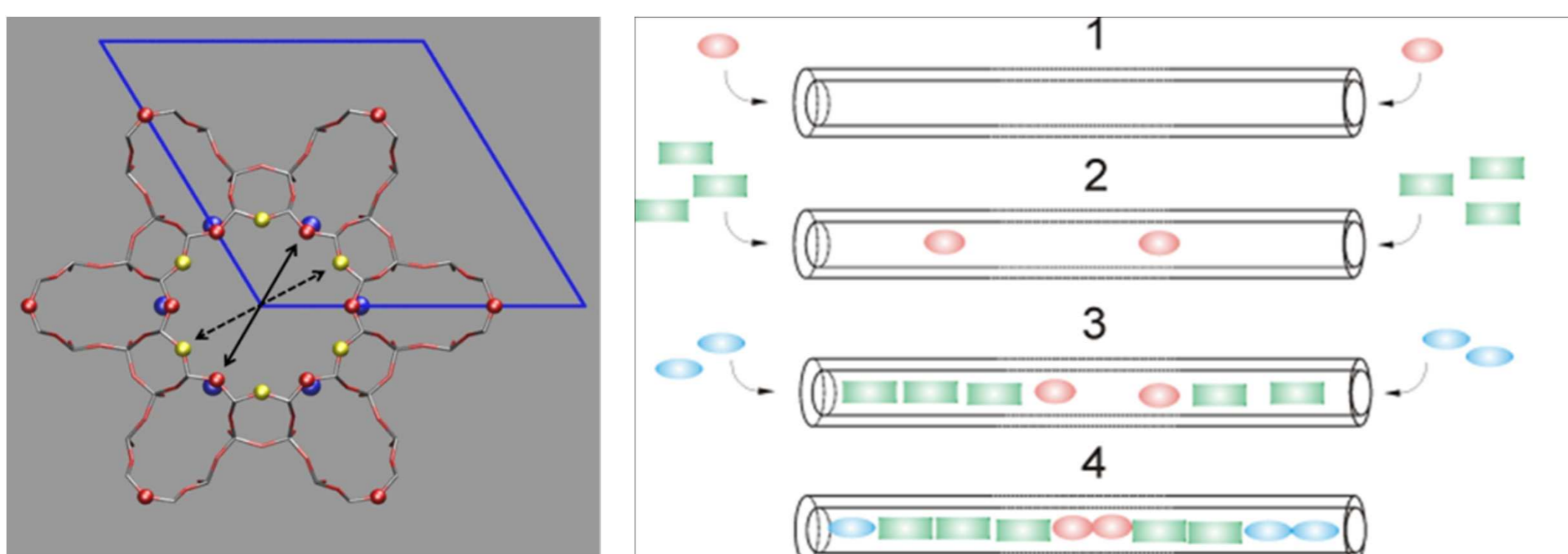
present:

At the entrance of zeolite nanochannels



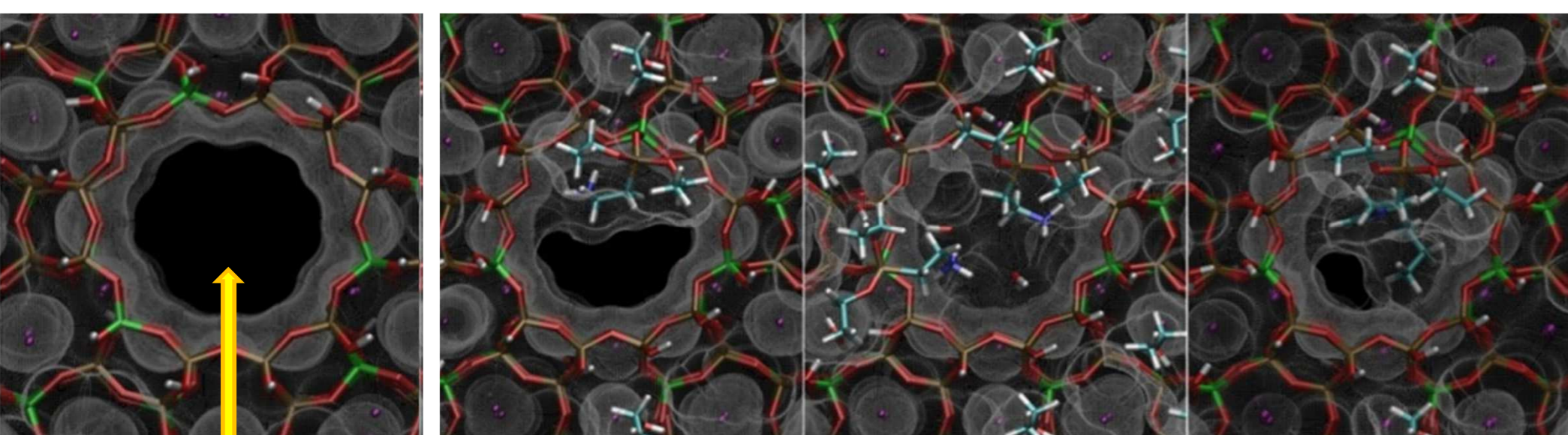
Zeolite L (ZL) frame and morphology

ZL entrances (2 per channel) are fundamental for ZL/dye assembly



Sequential assembly of 1-D supramolecular structures of dyes:
Many Applications!!!

ZL entrances can be functionalized *e.g.* to prevent (in/out) transit of molecules



Available space at ZL entrance

Covalent binding of alkoxy silane molecular stoppers allows to resize the ZL channel openings

- By condensing with OH groups at the channel entrance, stopper molecules irreversibly modify ZL. The channel entrance may be fully or partially blocked according to the stopper size:

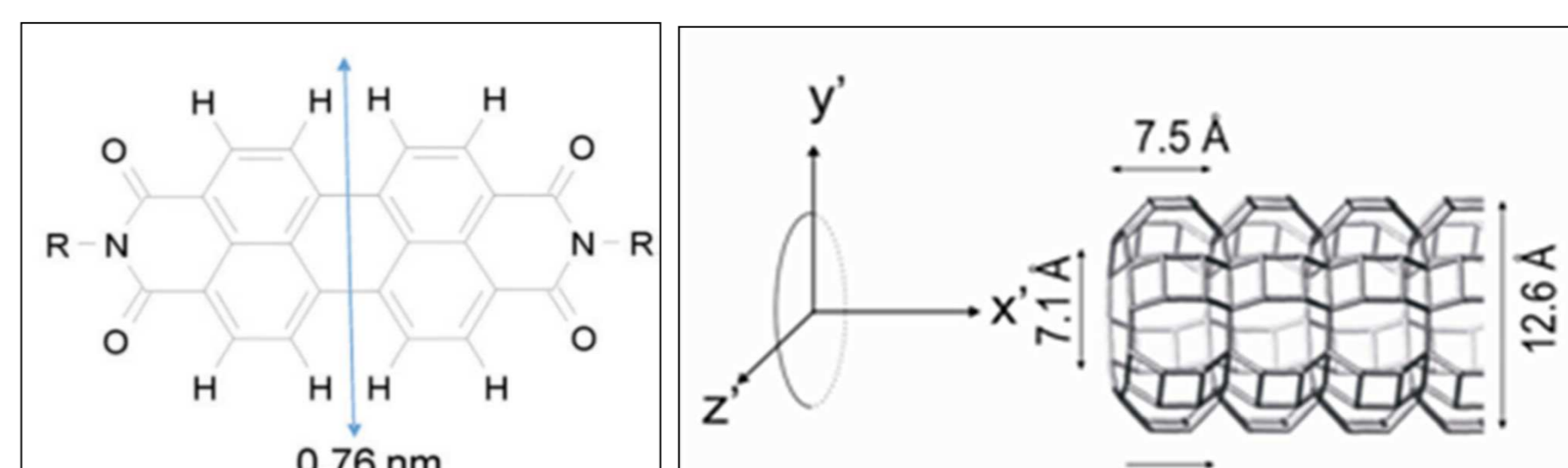
- Stoppers with **small tail groups** behave as partially opened lids. Two stoppers are needed to fully plug the channel entrance.

- Stoppers with **bulky tail groups** seal the entrance like a **cock**: full closure may be achieved with just one single stopper

Angew Chem Int Ed 2015, 54, 11112
doi 10.1002/anie.201504745

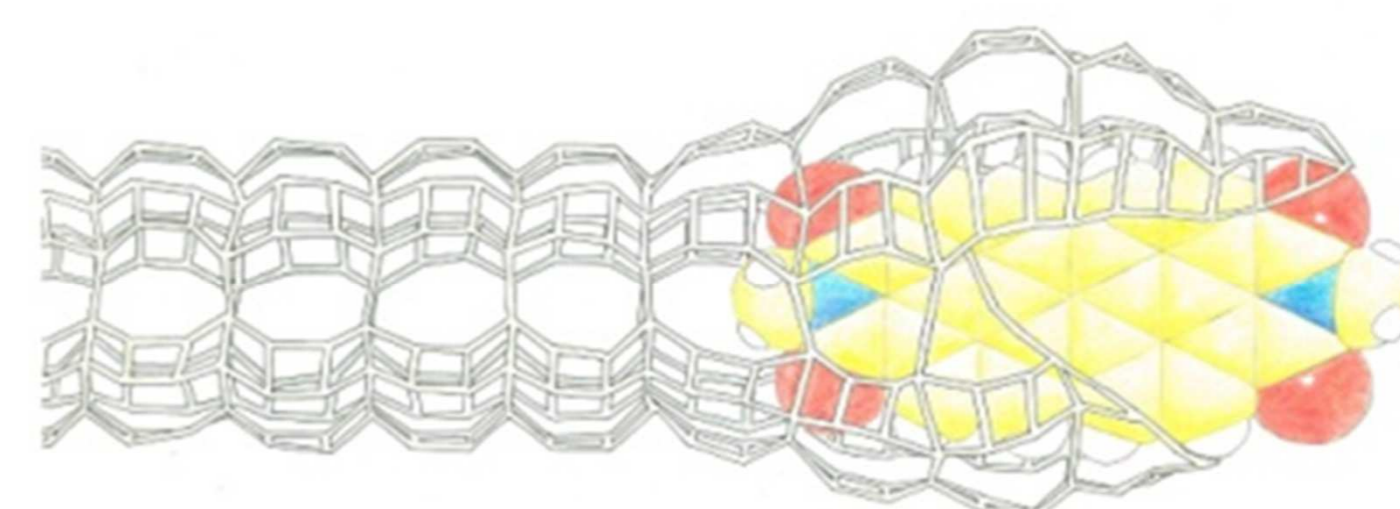
Even if perylene diimide (PDI) dyes are larger than ZL channel openings, many ZL/PDI hybrids are fabricated under vacuum at $T > 180^\circ$.

P.Cao et al., Chem.-Eur.J. 2016,22, 4046.

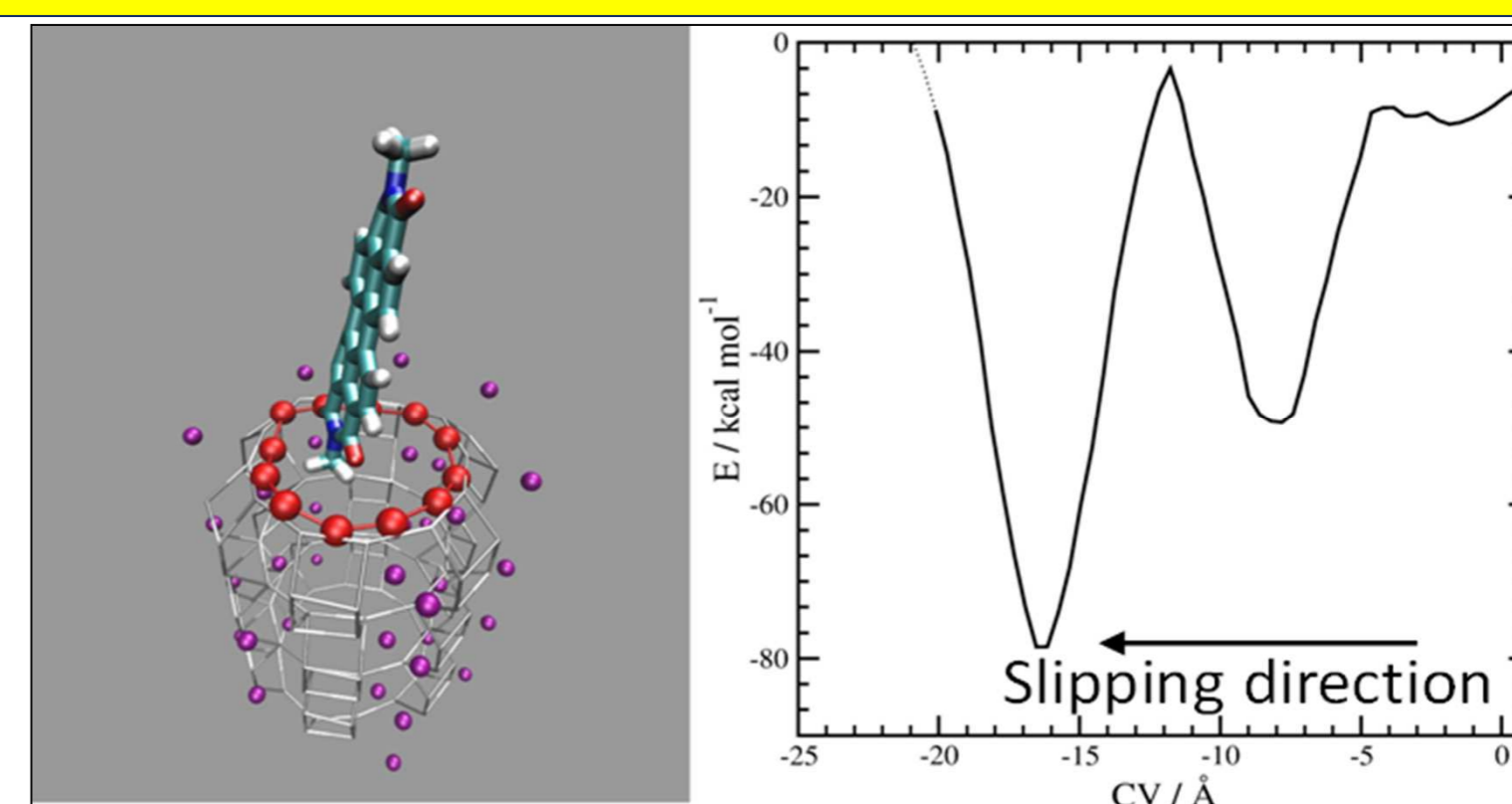


How can this be possible?

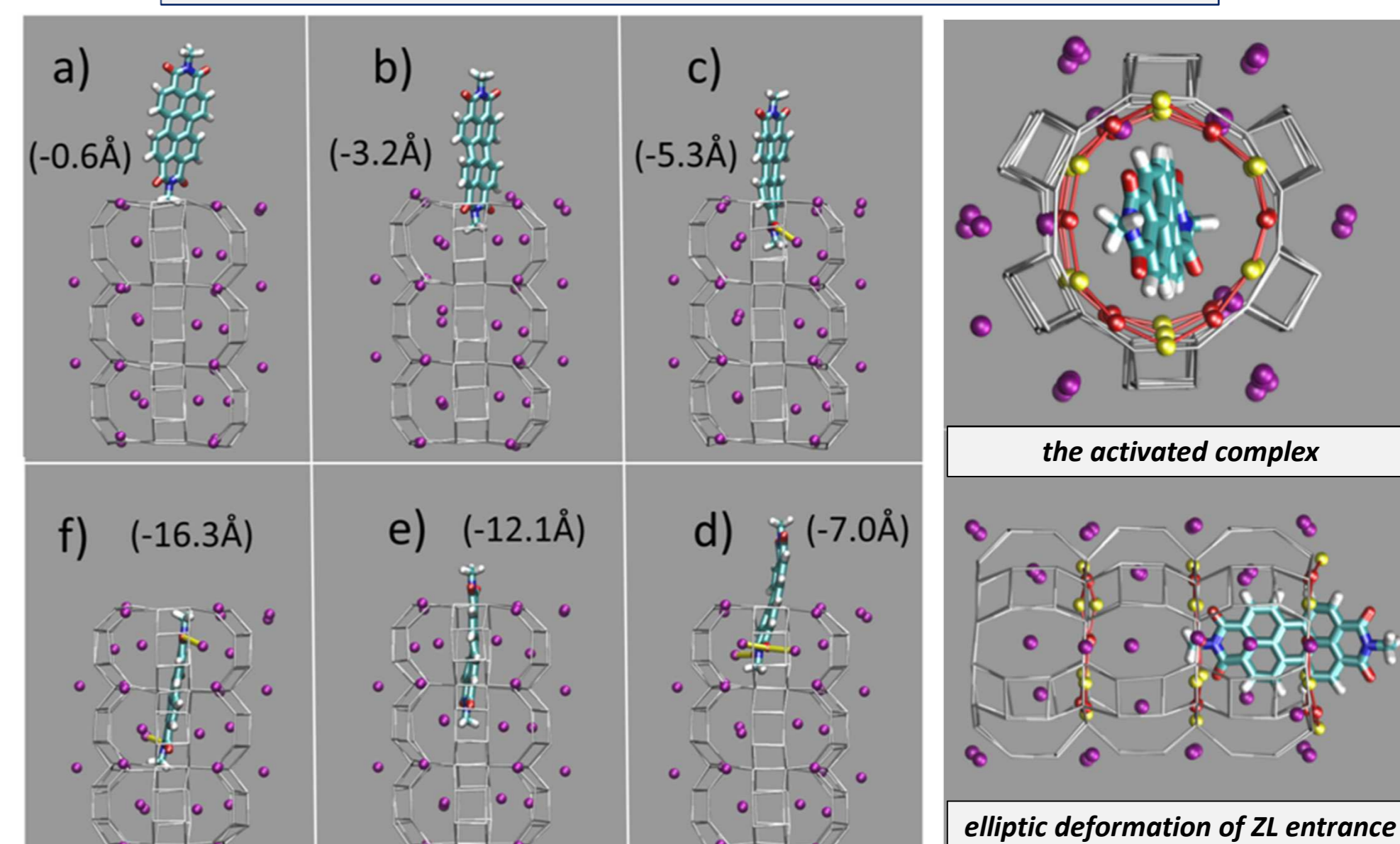
Correlated host-guest motions help bulky molecules to enter pores smaller than their size!



Indeed, like a snake is able to swallow a mouse although the mouse is too large, ZL can «swallow» molecules larger than its entrance!



Free energy profile for a PDI insertion in a ZL crystal



Why can bulky PDI molecules enter the ZL pores?

- Funnel-like shape of the ZL channel openings
- Stabilizing interaction between PDI carbonyl groups and ZL potassium cations
- Host/guest cooperative vibrational modes
- Asymmetry in the free energy profile (**unidirectional motion!**)

PDI entrance process favoured over PDI exit

ChemComm 2016, 52, 11195 doi 10.1039/c6cc05303c



The poster presents results of a cooperation between Gion Calzaferri (DCB, University of Bern) and Ettore Fois and Gloria Tabacchi Department of Science and High Technology, University of Insubria, and INSTM, Via Valleggio 9, I-22100 Como, Italy.

This information was presented at:

6th EuCheMS Chemistry Congress

Seville, 11-15th September 2016

OXIDE2016 VI International Workshop on Oxide-based Materials

Naples, 21-24th September 2016

XLIV Congress of the Physical Chemistry Division of the Italian Chemical Society

Naples, 20-23 September 2016

For more information and movies see:

<https://goo.gl/OWU2U0>

Fluorenone 2010

<https://goo.gl/jHQxsl>

Fluorenone Wesolowski 2013

<https://goo.gl/2yaJND>

Oxonine 2012

<https://goo.gl/OWU2U0>

Methilagridine 2013

<https://goo.gl/xBy8un>

stopcock 2015

<https://goo.gl/FaUB18>

stopcock 2015 (alternative link)

<https://goo.gl/T5bSL4>

How can a snake swallow a mouse bigger than its mouth? 2016