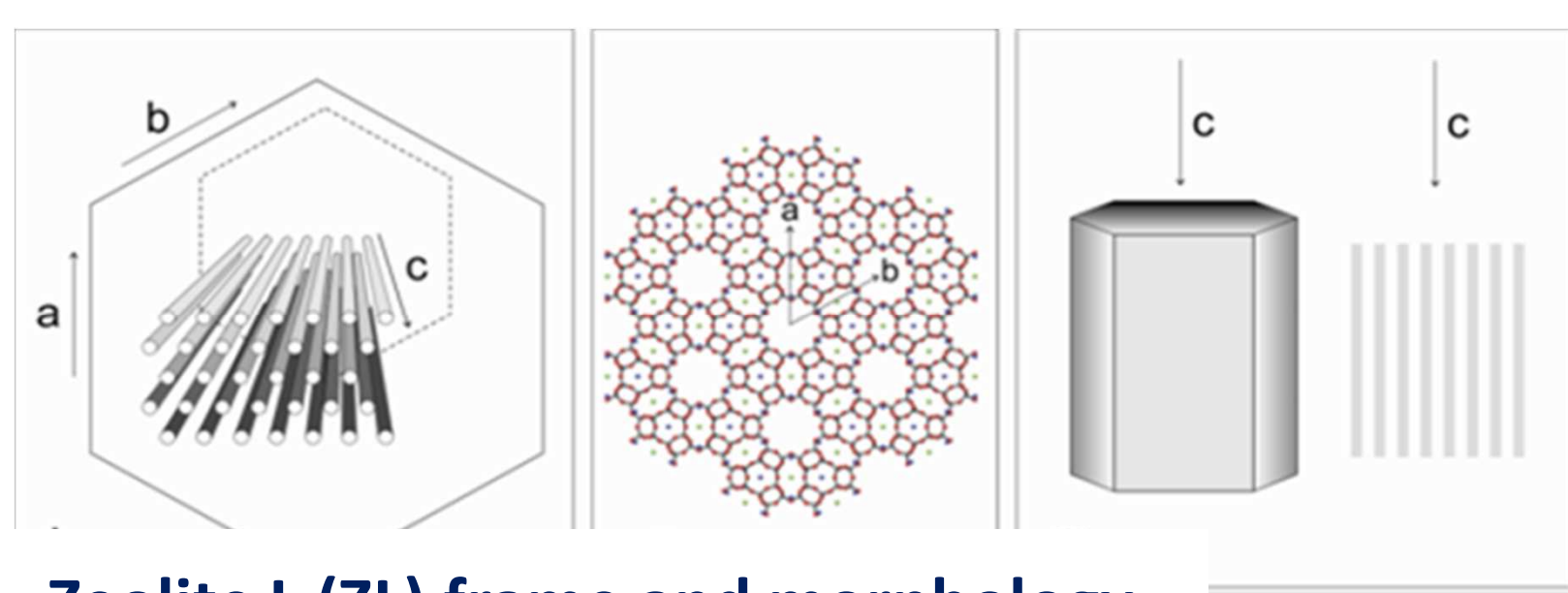
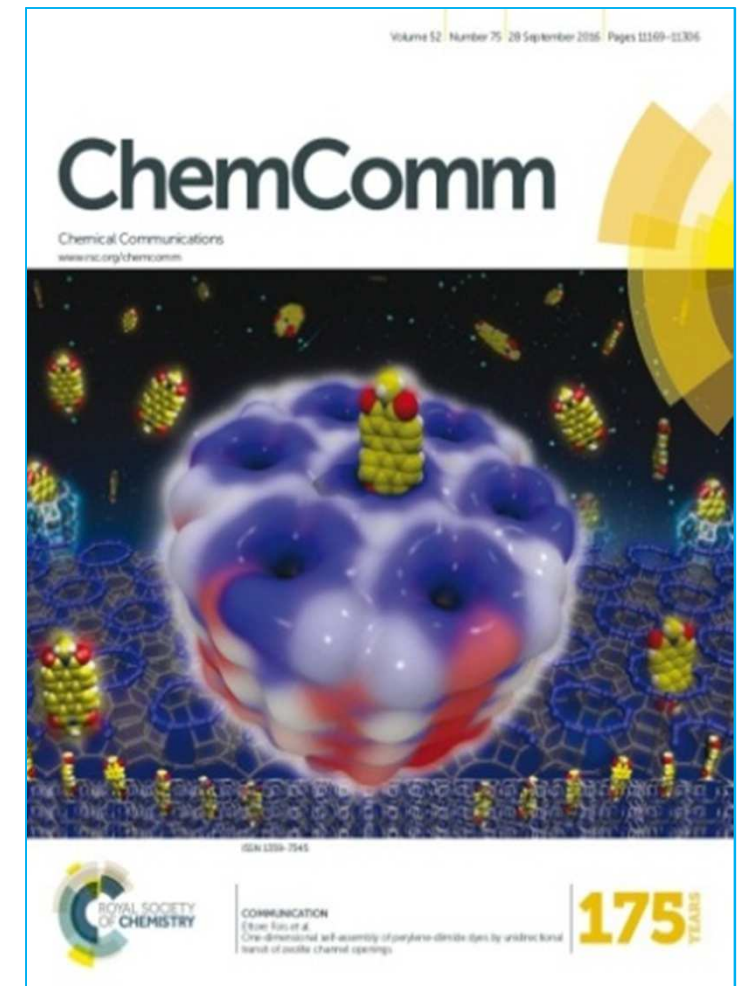


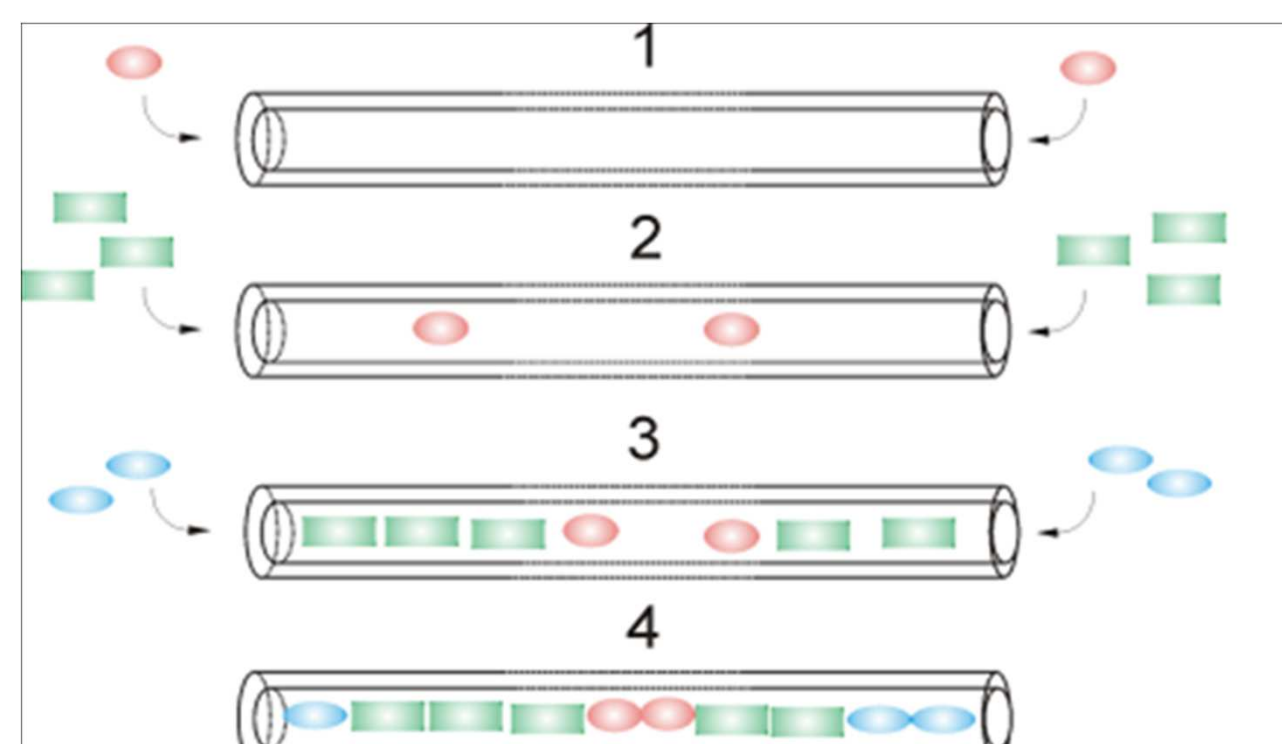
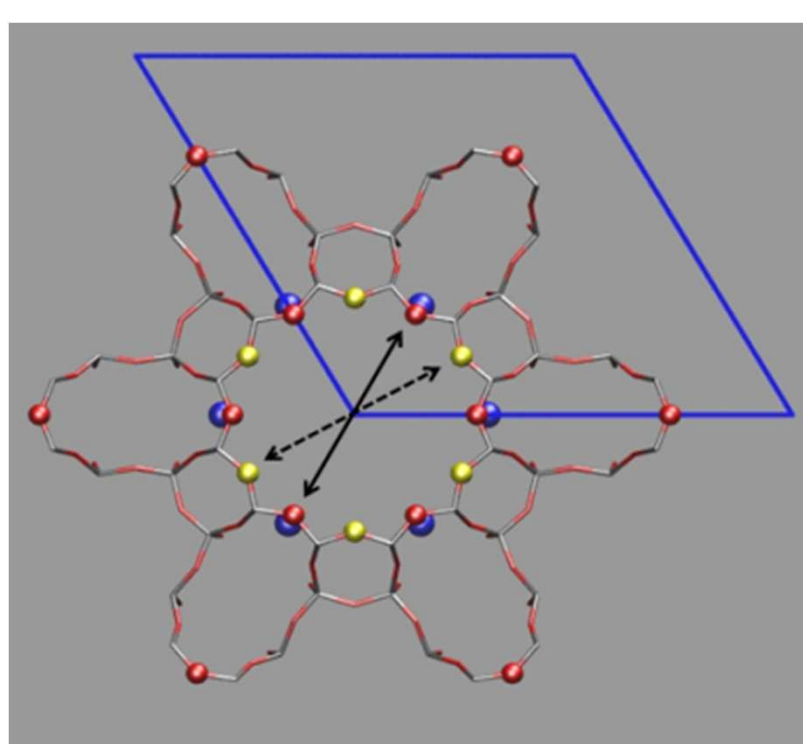
*present:*

# At the entrance of zeolite nanochannels



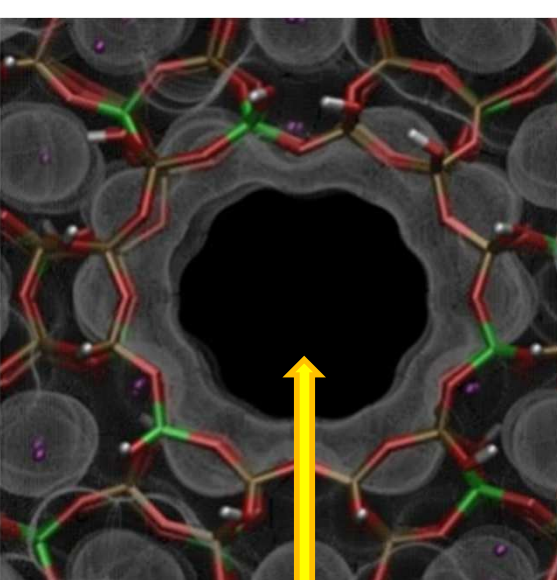
Zeolite L (ZL) frame and morphology

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

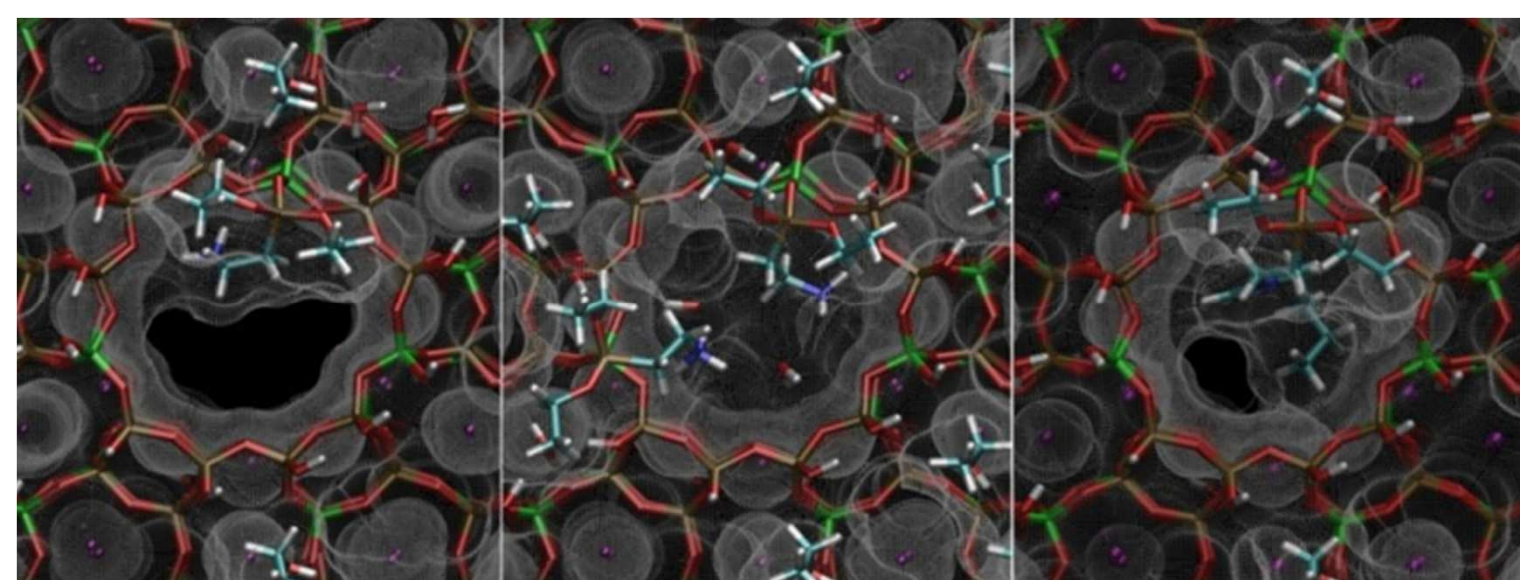


**Sequential assembly of 1-D supramolecular structures of dyes:**  
**Many Applications!!!**

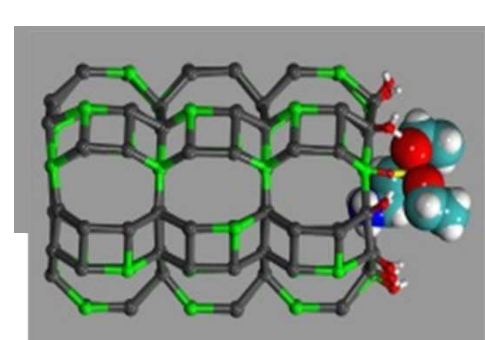
**ZL entrances can be functionalized *e.g.* to prevent (in/out) transit of molecules**



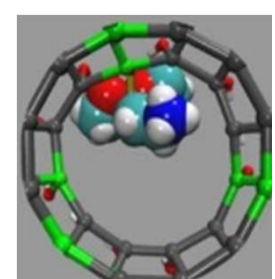
Available space at ZL entrance



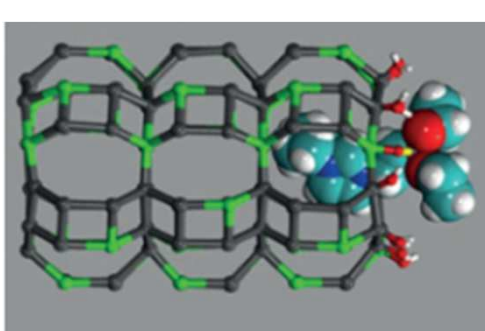
Covalent binding of alkoxy silane molecular stoppers allows to resize the ZL channel openings



- 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.

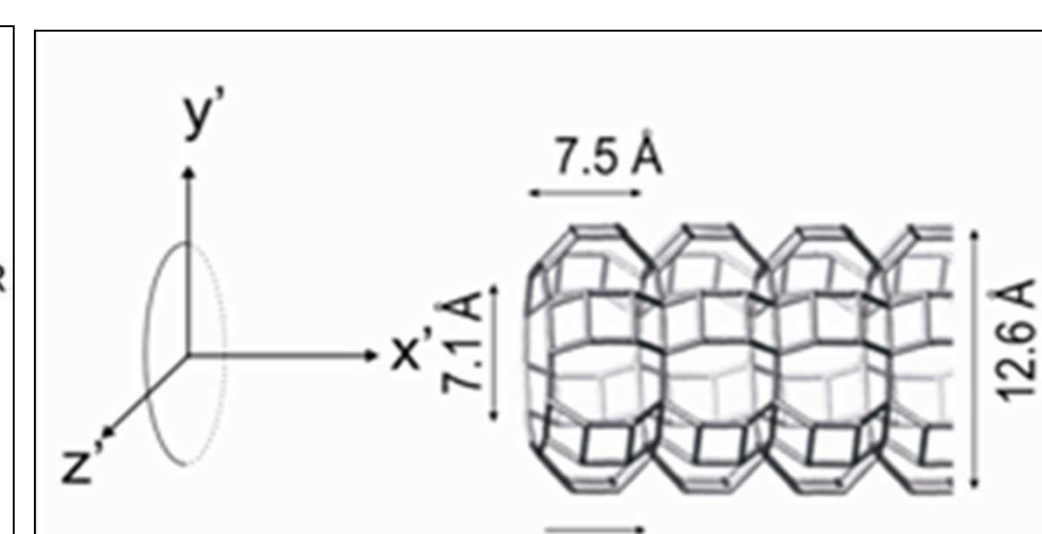
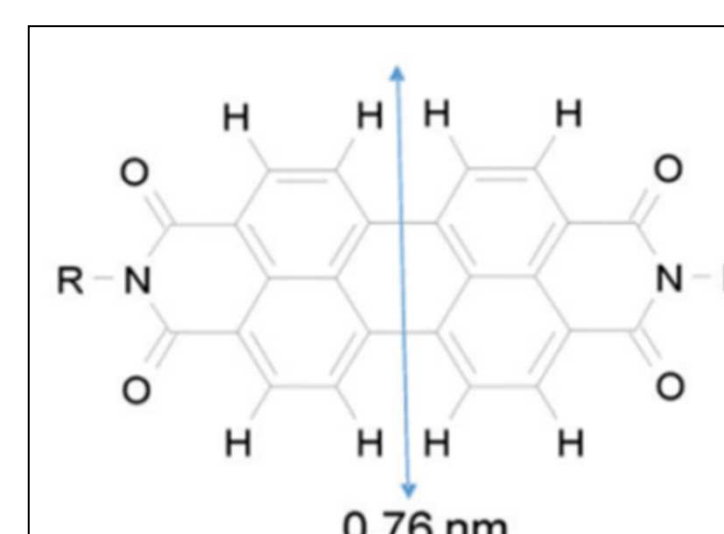


- Stoppers with **bulky tail groups** seal the entrance like a **cork**: full closure may be achieved with just one single stopper

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

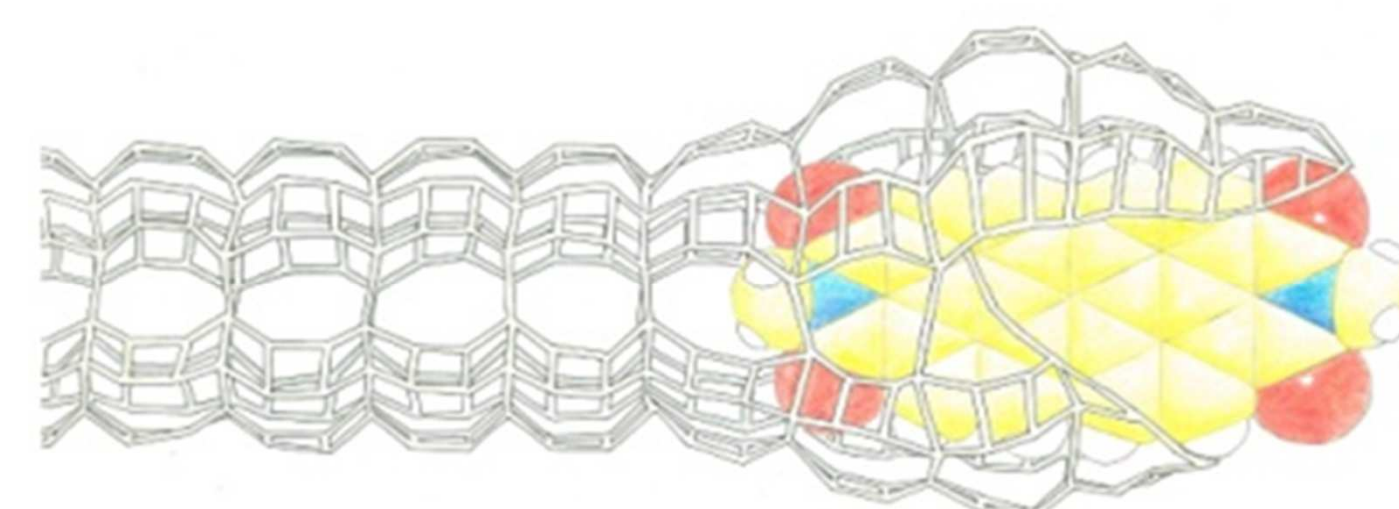
Even if perylenediimide (PDI) dyes are larger than ZL channel openings, many ZL/PDI hybrids are fabricated under vacuum at  $T > 180^\circ$ .

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

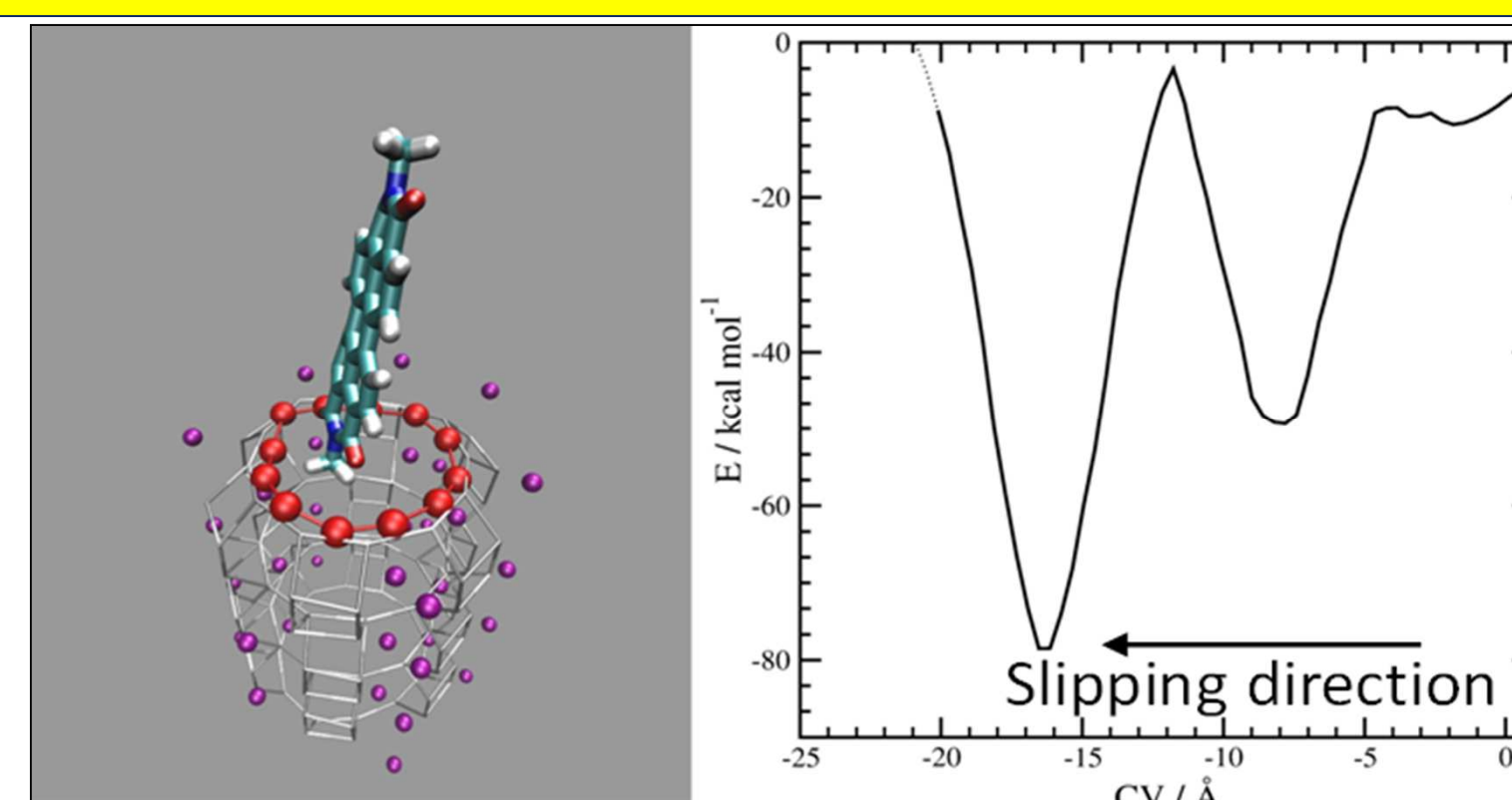


**How can this be possible?**

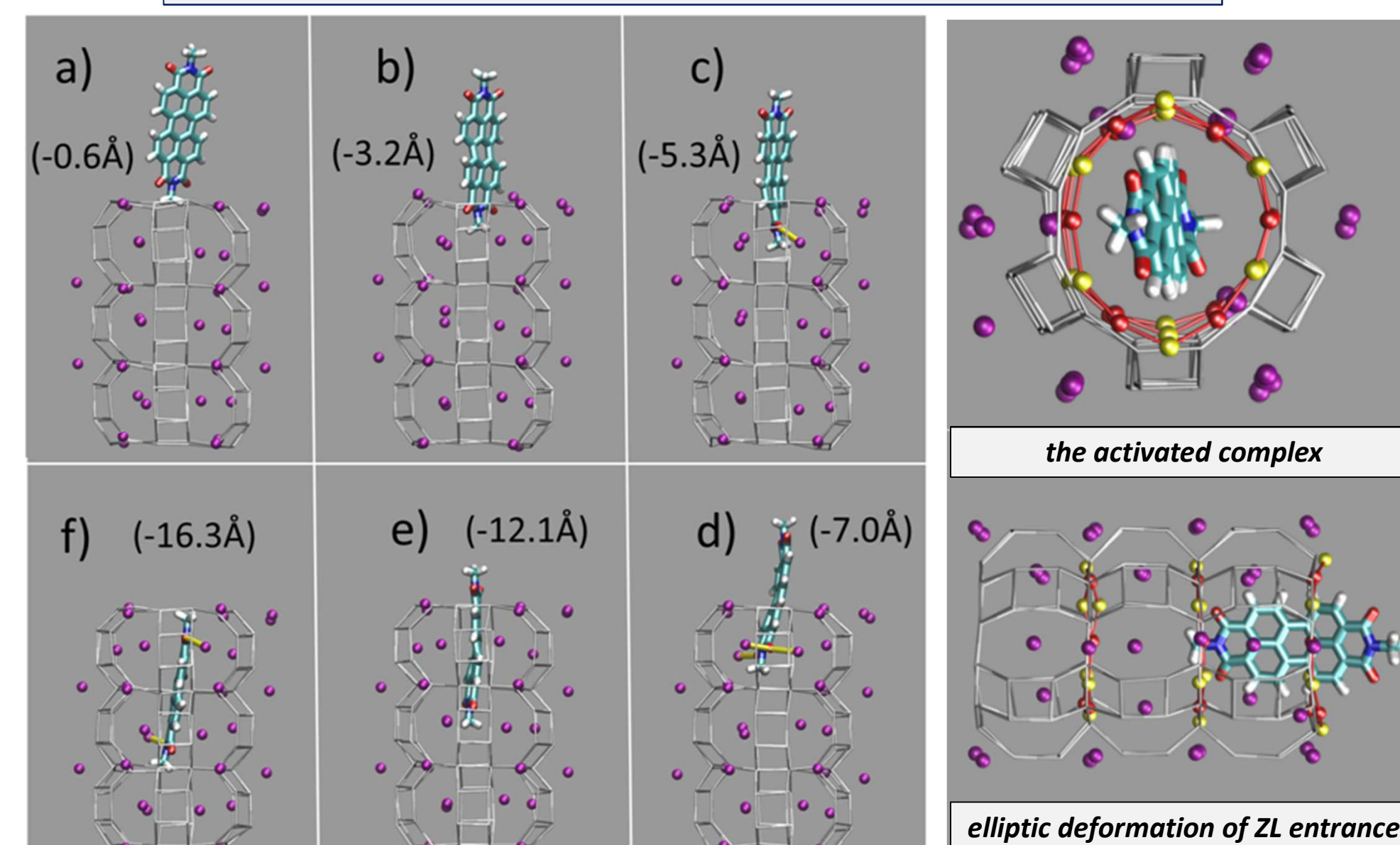
***Correlated host-guest motions help bulky molecules to enter pores smaller than their size!***



***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**

