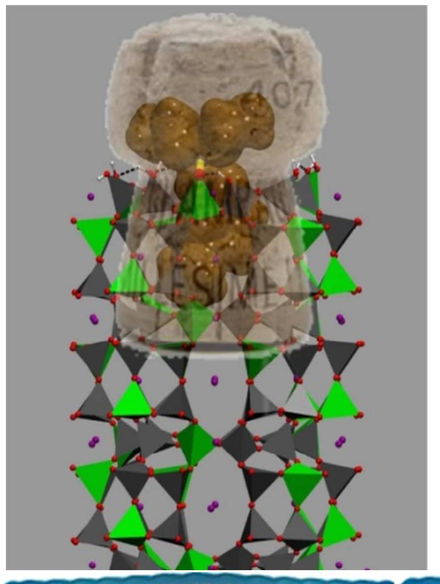

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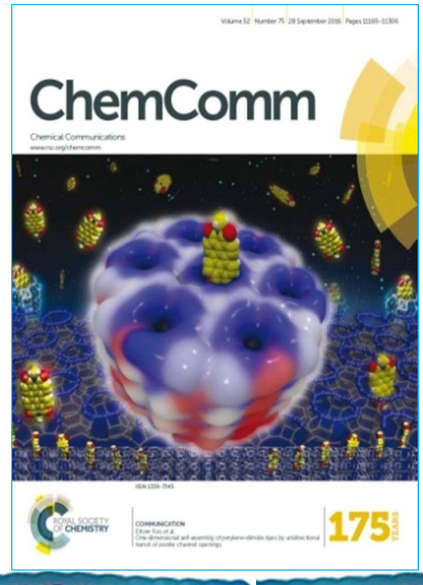
present:

At the entrance of zeolite nanochannels



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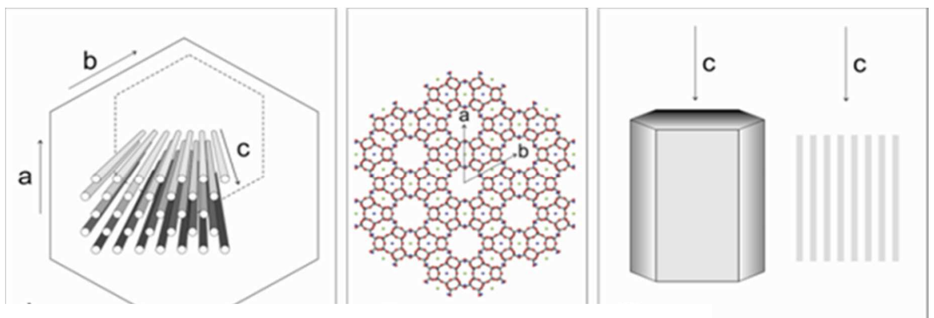
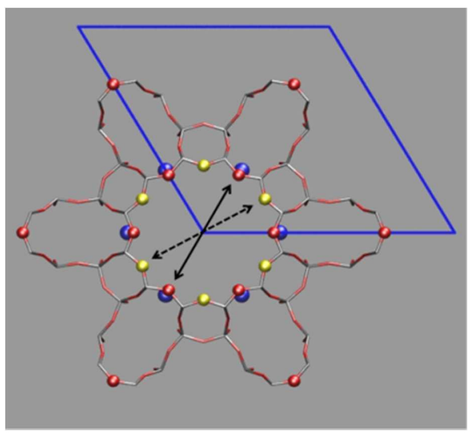
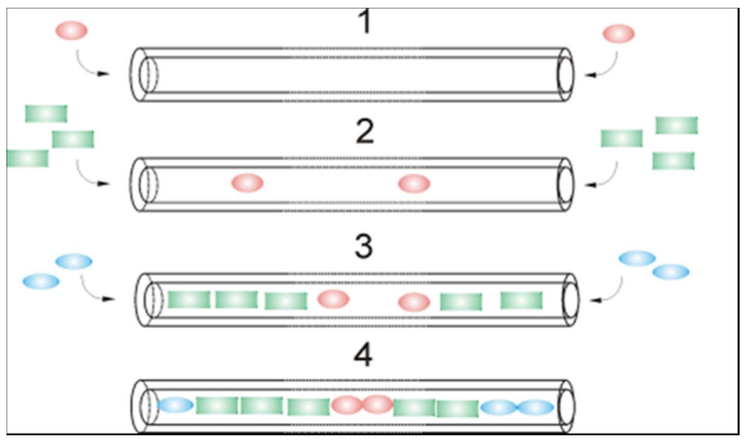


Zeolite L (ZL) frame and morphology

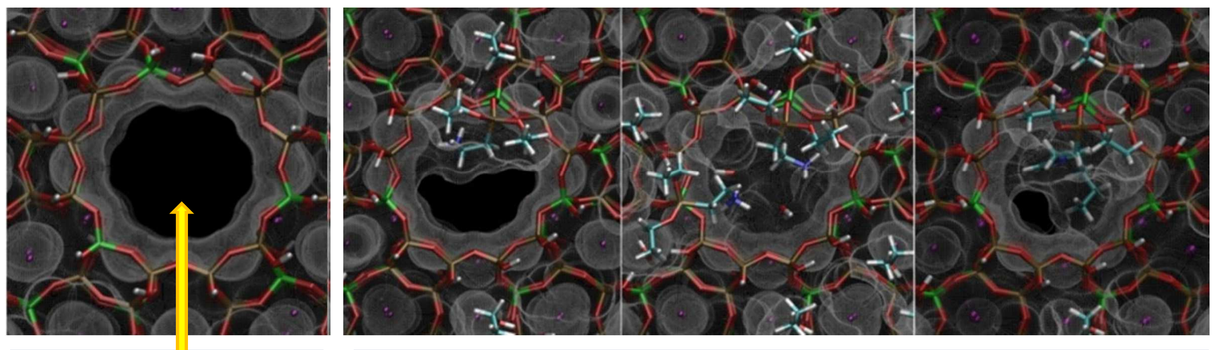
ZL entrances (2 per channel) are fundamental for ZL/dye assembly





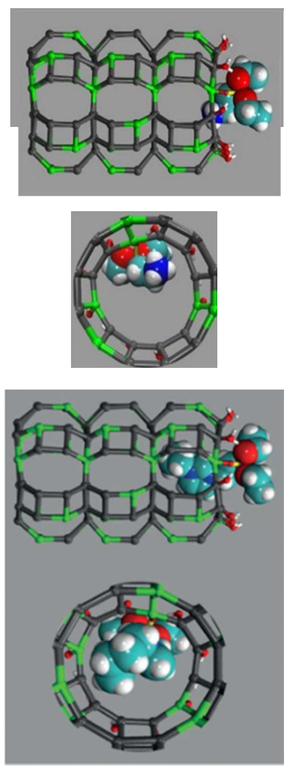
Sequential assembly of 1-D supramolecular structures of dyes: Many Applications!!!

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



Available space at ZL entrance

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

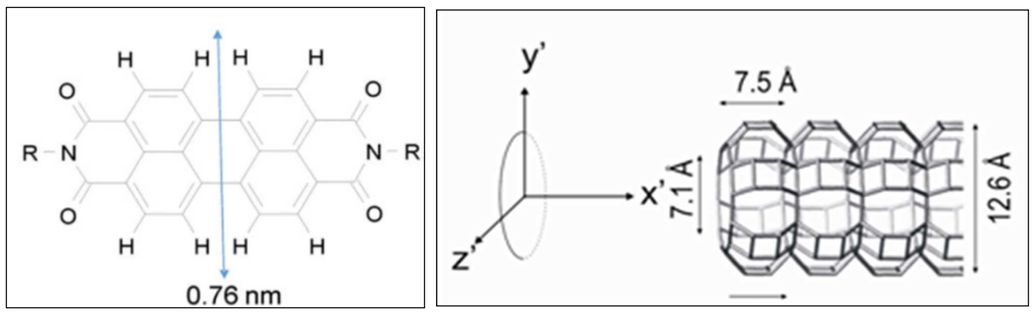


- By condensing with OH groups at the channel entrance, stopper molecules irreversibly modify ZL. The channel entrance may be fully or partially blocked according to the stopper size:
- Stoppers with **small tail groups** behave as partially opened **lids**. Two stoppers are needed to fully plug the 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

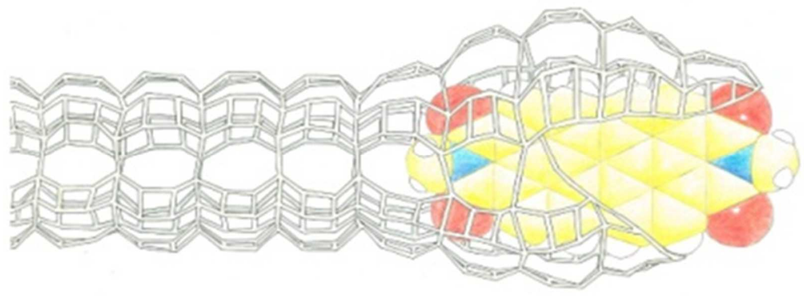
Even if perylenediimide (PDI) dyes are larger than ZL channel openings, many ZL/PDI hybrids are fabricated under vacuum at T> 180°.

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

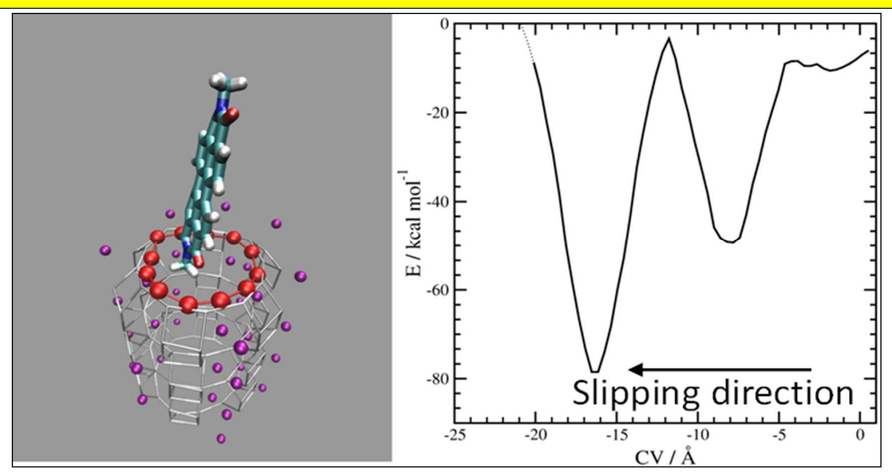


How can this be possible?

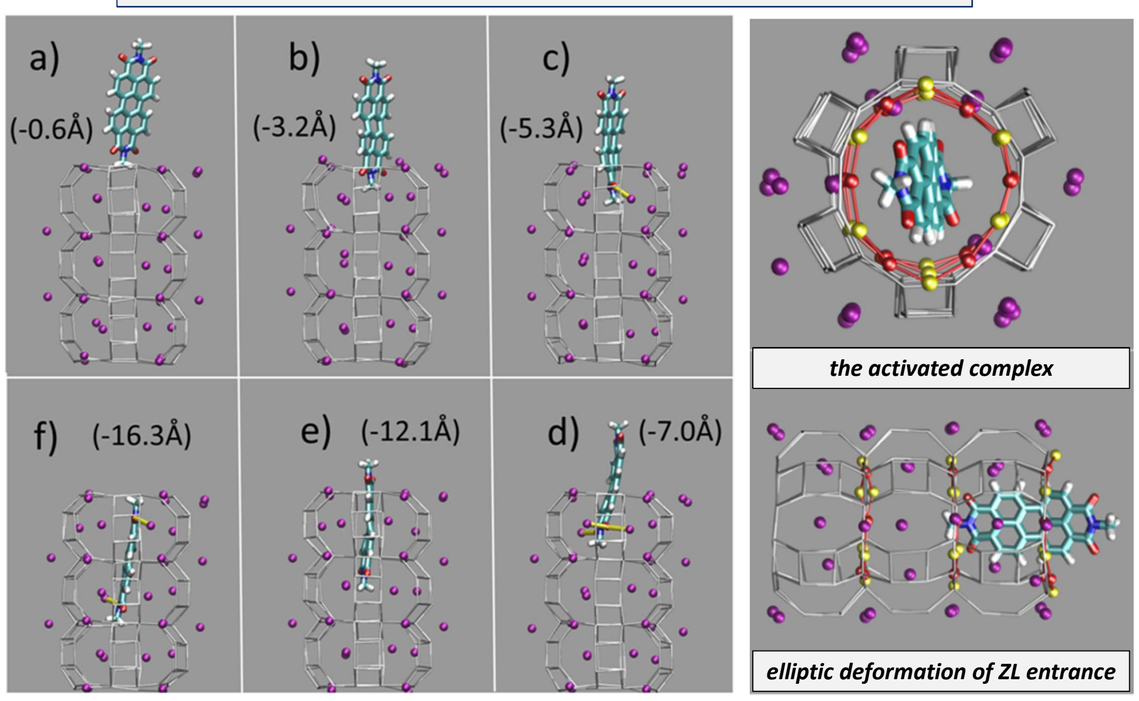
Correlated host-guest motions help bulky molecules to enter pores smaller than their size!



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

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