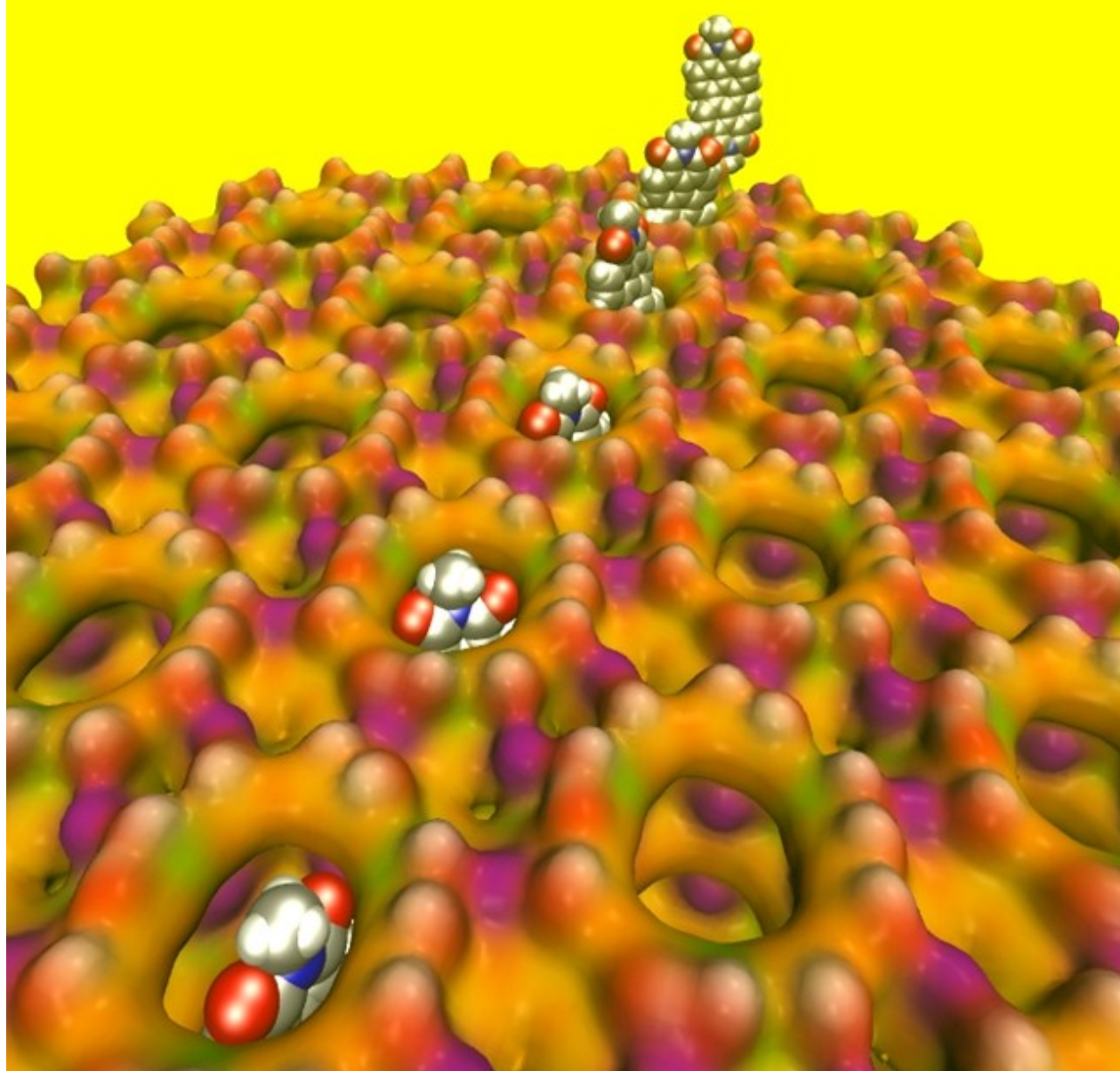


ELECTRONIC SUPPLEMENTARY INFORMATION

**One-Dimensional Self-Assembly of Perylene-Diimide Dyes by
Unidirectional Transit of Zeolite Channel Openings**

Gloria Tabacchi, Gion Calzaferri and Ettore Fois*



1. Model and Methods

The slipping of a dye of the perylene diimide (PDI) family into the Zeolite L (ZL) channel opening was studied via a periodic slab approach adopting a metadynamics sampling combined with first principles molecular dynamics. The slab model was essentially the same as in Ref. (1), and was built by cutting a slab from an optimized anhydrous ZL structure, with a 3/1 Si to Al ratio and a hexagonal unit cell of stoichiometry $K_9[Si_{27}Al_9O_{72}]$. The ZL cell parameters were $a=b=18.466 \text{ \AA}$, $c=7.476 \text{ \AA}$, $\gamma=120^\circ$, which are the cell parameters of a fully dehydrated K-LTL zeolite (with a Si/Al ratio of 2.87) at room temperature conditions (2). The slab consists of three ZL unit cells along the c axis. The Al-O and Si-O dangling bonds resulting from the cut were saturated with H atoms, thus forming surface silanol groups. The stoichiometry of the slab is $K_{30}[Si_{90}Al_{30}O_{252}H_{24}]$. Periodic boundary conditions were applied in 3-dimensions, by adopting a computational cell with parameters $a=b=18.466 \text{ \AA}$, $c=48.0 \text{ \AA}$, $\gamma=120^\circ$. The size of the c parameter allows for about 25 \AA vacuum among images along the z direction. Graphical representations of the slab are reported in Figure S1. The total charge of the system is zero. With such a geometry set up, there are two open surfaces, both with the 12-membered ring opening typical of ZL. Each surface is characterized by the presence of 12 OH groups, some belonging to Al-centered sites, other to Si-centered sites. On each open surface of the slab, 6 OH groups are on the verge of the channel entrance.

The dye used in the simulation (see Figure S2) represents a typical member of the PDI family, with two methyl groups bonded to the N atoms of the perylene diimide core. The PBE approximation to Density Functional Theory⁽³⁾ was adopted for the electronic structure calculations, electron-nuclei interactions were dealt with via pseudopotentials: they were of the ultra-soft type for C, N, O, H atoms,⁽⁴⁾ while norm-conserving pseudopotentials were adopted for K (semi-core), Al and Si.⁽⁵⁾ Electronic states were expanded in a planewaves basis set up to a kinetic energy cutoff of 25 Ry, while electronic density was represented up to a cutoff of 200 Ry. Only the Γ point of the Brillouin zone was considered in all the calculations. Such a computational scheme for electronic structure treatment has been proved to properly describe large sized inorganic-organic systems including dye-zeolite hybrids (see ref. 8 in the main text).

The Car-Parrinello⁽⁶⁾ equations of motion were integrated with a time step of 5 au and an inertia parameter for the electronic coefficients of 500 au. Nosè-Hoover thermostats were connected to the ionic degrees of freedom, with a target temperature of 473 K (200°C). All atoms were free to move with the exception of three silicon atoms on the bottom plane of the slab (see Figure 3, in the main text). The metadynamics⁽⁷⁾ run was performed by adopting, as collective variable CV, the average displacement, along the c axis, of all the carbon atoms of the PDI core with respect to the 12 oxygen atoms of the channel opening (see Figure S1, and Figure 1 in the main text). The metadynamics

equations were integrated by adopting the Langevin formalism, using a friction $\gamma=0.001$, and with Gaussian hills of width and height of 0.12 and 0.005 au, respectively. The CV was allowed to vary between +1.0 Å to -20.0Å, with respect to the reference configuration (Figure S1c). The slipping was completed in about 2000 metadynamics steps, corresponding to 400000 first principles molecular dynamics steps. The Vreco code (see www.cpmc.org) was used to reconstruct the free energy profile.

Also, few geometry optimizations were performed via a quasi-Newton approach and stopped when maximum forces on atom positions were below 5×10^{-4} hartree/bohr. All calculations were performed with the CPMD code.⁽⁸⁾

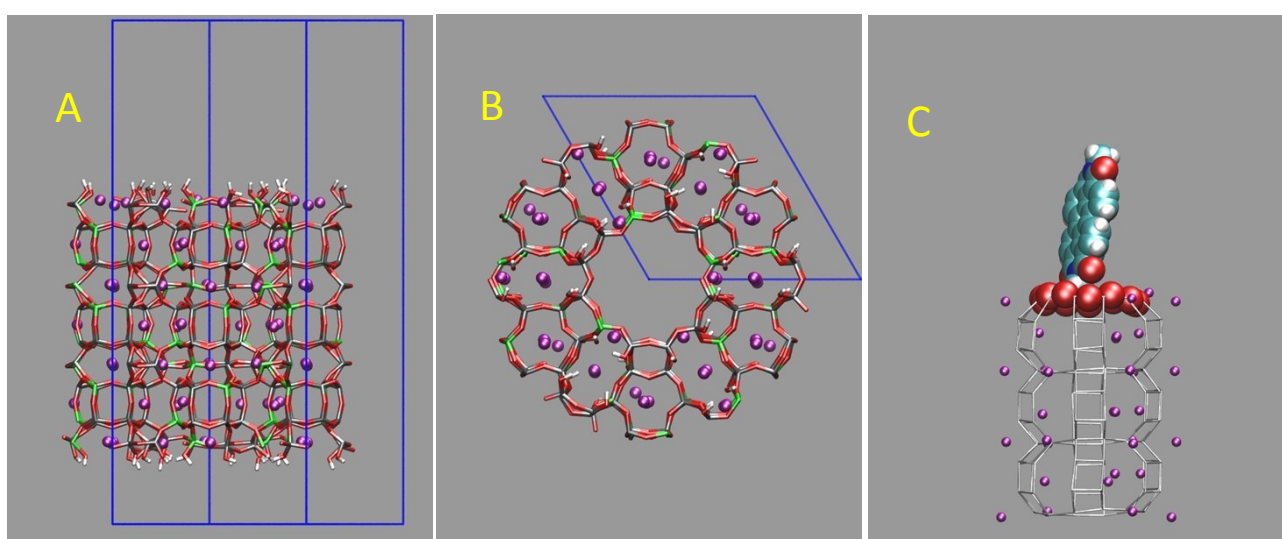


Figure S1. (A): Graphical representation of the optimized structure of the empty 3-unit-cell ZL model slab; projection perpendicular to the (001) plane. (B), same structure as A, projected on the (001) plane. The simulation cell is highlighted with blue lines. Atoms color code: brown, Si; green, Al; red, O; purple, K; white, H. (C) Graphical representation of the reference structure for the metadynamics simulation. Only the Si/Al atoms of the framework (gray sticks) are shown, K^+ cations are represented as purple spheres. The PDI molecule is represented as vdW spheres (C=cyan, O=red, N=blue, H=white). The 12 O atoms of the 12-membered ring involved in the CV definition are represented as red vdW spheres.

2. Size and structure of the guest molecule (PDI)

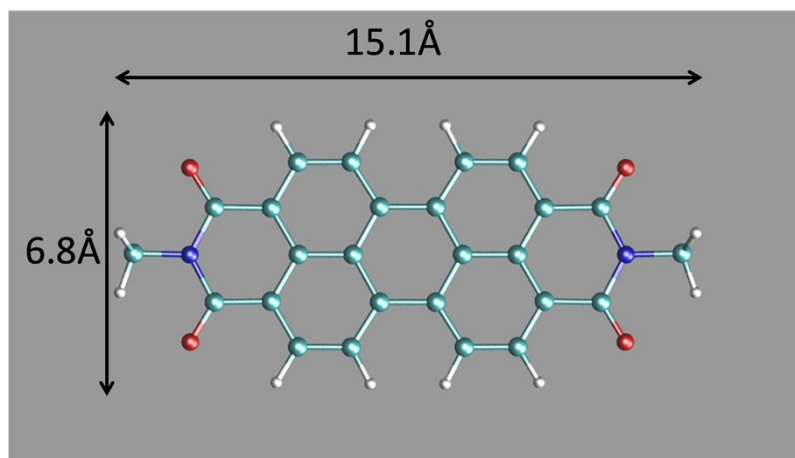


Figure S2. Graphical representation of the optimized PDI structure adopted in this study. Atom color code: C, cyan; H, white; N, blue; O, red. The geometry optimizations for the PDI structure was carried out with the same set up as for the full system, but by adopting an isolated cubic box of 45 Å side. The distances in the picture are nuclei-nuclei separations and do not include vdW radii contributions.

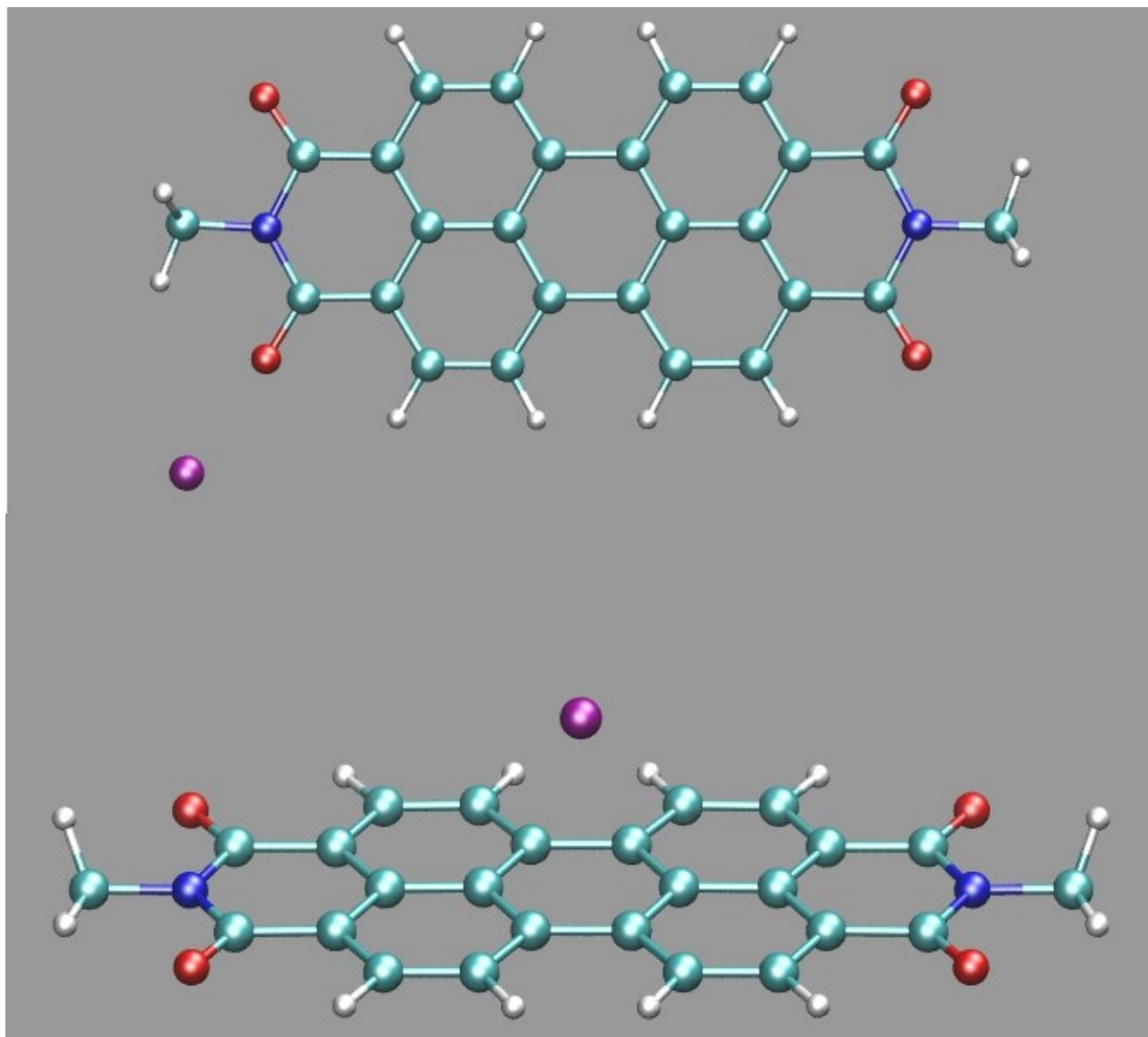


Figure S3. Graphical representations of the two main types of K^+ -PDI interactions. Top: planar structure featuring the interaction of a K^+ with one carbonyl oxygen atom. Bottom, structure featuring the charge- π interaction, with the K^+ cation on top of the central ring of the perylene core. Atom color code: K, purple; C, cyan; H, white; N, blue; O, red. The geometry optimizations for the K^+ -PDI interactions were carried out with the same set up as for the full system, but by adopting an isolated cubic box of 45Å side.

3. Structural details of the ZL channel openings.

The values of the O1-O1 and O2-O2 diameters obtained by diffraction studies of ZL samples, characterized by slightly different Si/Al ratio, water content and extra-framework cations are reported in Table S1. The corresponding values of the cell parameters (in Å), the number of water molecules per unit cell, the cation (Na or K) content, the Si/Al ratio and the temperature (in °C) are also reported in Table S1.

The values of the O1-O1 and O2-O2 diameters of different 12M rings as a function of their distance from the channel entrance (see Figure 3, main text) obtained in the present study and discussed in the main text, were calculated from the minimum energy structure of the empty ZL model and are reported in Table 1 of the main text (only the average values) and in Table S2 (all values)

Table S1. O1-O1 and O2-O2 diameters (in Å) from different diffraction studies. The entries refer to the extraframework ions (Na/K) content, the temperature, the water content, the O1-O1 and O2-O2 diameters the a, c cell parameters and the Si/Al ratio. The values in parentheses are the O1-O1 and O2-O2 diameters (in nm) taking into account an oxygen radius of 1.35 Å (see www.iza-online.org).

Na/K	T(°C)	nH ₂ O	O1-O1	O2-O2	a	c	Si/Al
5Na ⁺ ;4K ⁺ (ref a)	25	21	9.840 (0.714)	10.492 (0.779)	18.40	7.52	3
9K ⁺ ; (ref b)	25	19	9.879 (0.717)	10.268 (0.757)	18.3367	7.5176	3.29
9K ⁺ (ref b)	244	0	10.081 (0.738)	10.407 (0.771)	18.3968	7.5019	3.29
9K ⁺ (ref c)	25	0	10.171 (0.747)	10.612 (0.791)	18.4660	7.4763	2.87

a) R.M. Barrer, H. Villinger, *Z. Kristallogr.* **1969**, 128, 352-370

b) L. Gigli, R. Arletti, S. Quartieri, F. Di Renzo, G. Vezzalini, *Microp. Mesop. Mater.* **2013**, 177, 8-16

c) J.M. Newsam, *J. Phys. Chem.* **1989**, 93, 7689-7694

Table S2. Values (in Å) of the O1-O1 and O2-O2 diameters of different 12M rings as a function of their distance from the channel entrance (see Figure 3, main text), obtained from the minimum energy structure of the empty slab. The average values of these distances, reported in Table 1 of the main text, are also reported here for comparison (see columns 2 and 6, labeled (av)). The entry labeled ∞ refers to an optimized periodic ZL crystal with Si/Al ratio of 3 and cell parameters a=b=18.466 Å and c=7.4763 Å. The values in parentheses are the O1-O1 and O2-O2 diameters (in nm) taking into account the O radius of 1.35 Å.

	O1-O1 (av)	(O1-O1) _a	(O1-O1) _b	(O1-O1) _c		O2-O2 (av)	(O2-O2) _a	(O2-O2) _b	(O2-O2) _c
1 st	10.338 (0.764)	10.782	10.132	10.101		10.649 (0.795)	10.920	10.521	10.505
2 nd	10.048 (0.735)	10.142	10.107	9.896		10.547 (0.785)	10.732	10.553	10.357
3 rd	10.067 (0.737)	10.103	10.079	10.020		10.501 (0.780)	10.559	10.521	10.422
∞	10.015 (0.732)	10.189	9.951	9.905		10.475 (0.778)	10.573	10.459	10.392

4. The flexibility of the PDI molecular structure

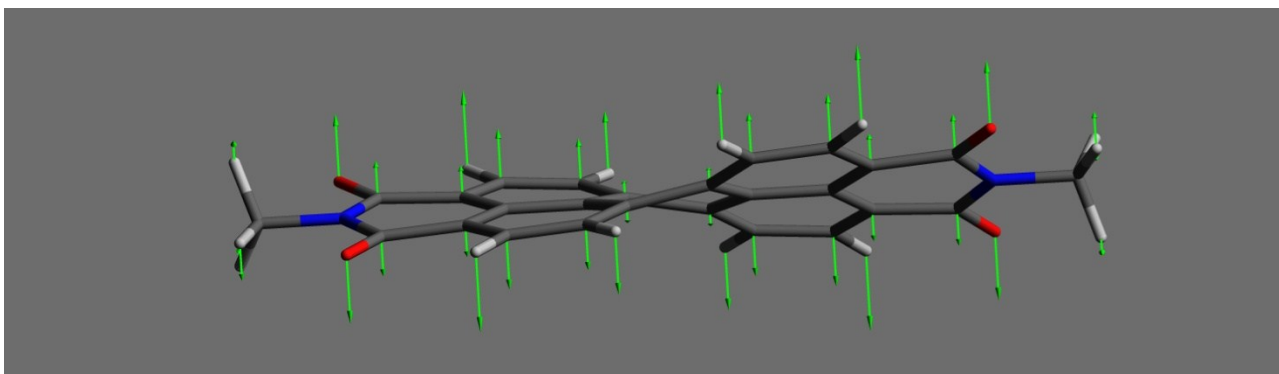


Figure S4. Graphical representation of the lowest energy vibrational mode of the PDI molecule. The green arrows indicate the displacement vectors of the mode.

5. Further details of the encapsulation process of PDI in zeolite L.

During the transit of the PDI from the 1st to the 2nd cell, i.e. at the maximum of the free energy profile, a K⁺ cation moves from its site (Fig. S5a) to an adjacent one (see Movie and Fig. S5), and, as a net result, the PDI central aromatic core becomes sandwiched between 2 K⁺ on opposite sides of the channel and aligned to one O2-O2 diameter (Fig. S5d), thus suggesting a charge- π -charge stabilizing interaction.

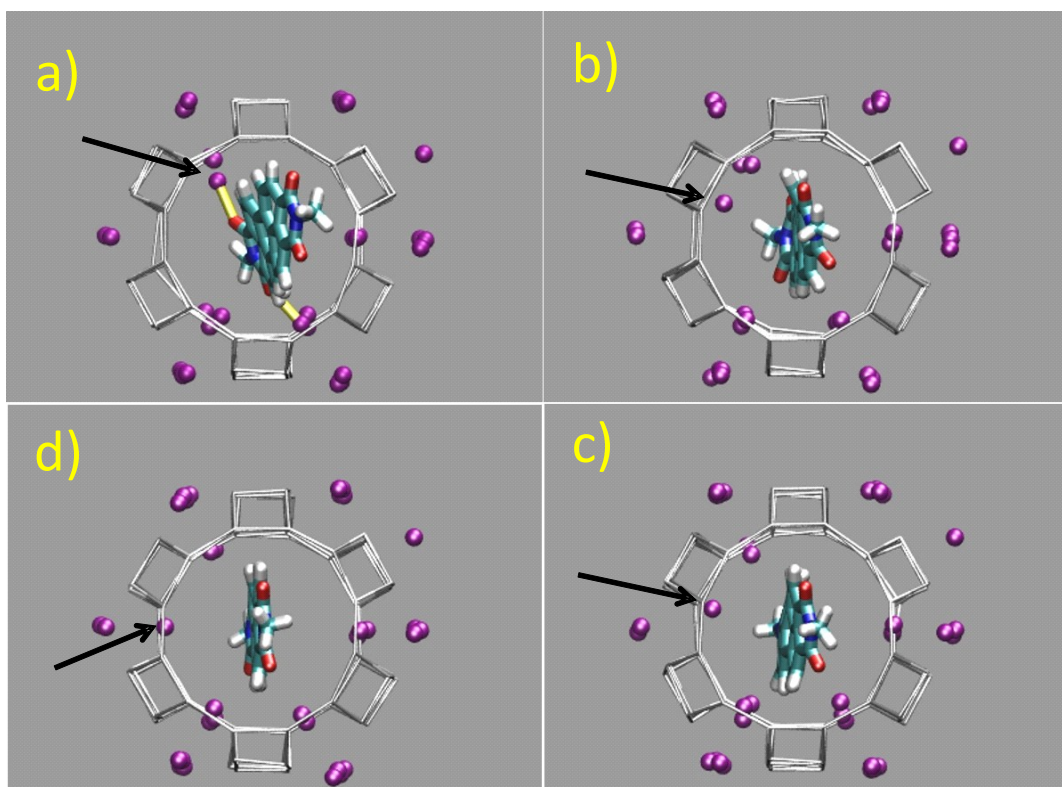


Figure S5. Series of snapshots (clockwise from a to d) representing the displacement of one K⁺ (indicated by the arrows, from one cage to an adjacent one). Color codes as in Fig. 2 of the main text.

This event may occur because the hypothetical optimal host-guest configuration, featuring the 4 carbonyl groups of PDI interacting with 4 K^+ of the zeolite, is prevented by a distance mismatch. In fact, the distance between the carbonyl oxygens along the long molecular axis, 11.35 Å, is not commensurate with the separation of 2 K^+ along the channel walls, which corresponds to the cell parameter c , 7.5 Å. Hence, the molecule continuously switches between diverse binding modes to try to maximize the $K^+ \cdots O=C$ interactions, see Movie and Fig. S6. For example, a single carbonyl oxygen of the PDI may be coordinated to 2 K^+ (Fig. S6, left), or, alternatively, two carbonyl groups may bind to two K^+ cations localized in adjacent cells, on opposite sides of the inner walls of the ZL channel (Fig. S6, right). The latter configuration is one of the most frequently visited binding modes: in this situation, the PDI long axis is not aligned with the channel axis. Configurations where PDI features a combination of these binding modes were detected as well. In these cases, two carbonyl groups may be coordinated to three distinct cations K^+ .

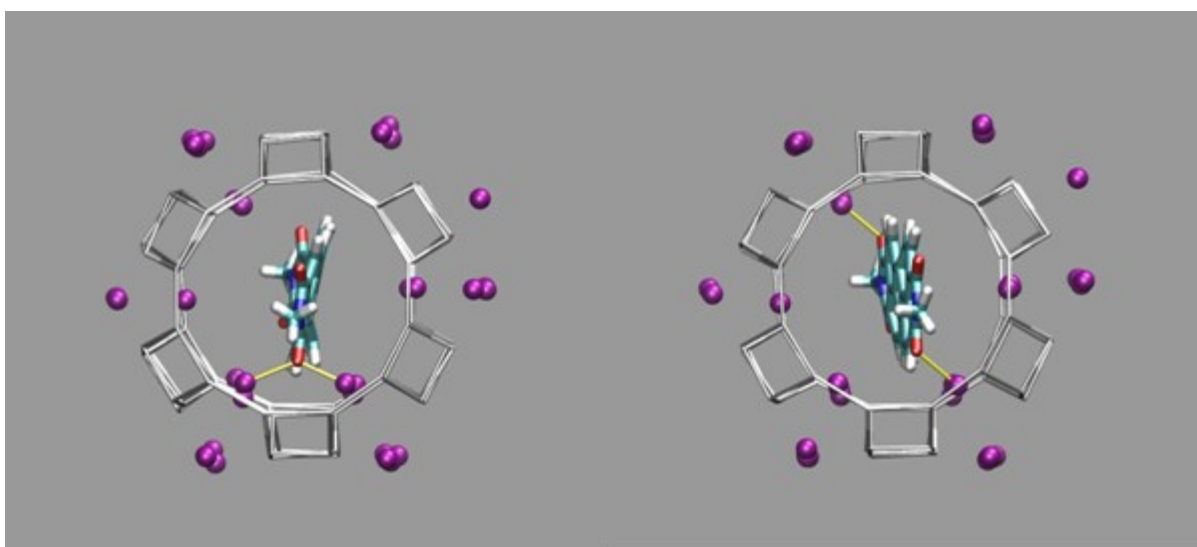


Figure S6 Projections along the channel axis c of 2 representative snapshots extracted from the metadynamics simulation, showing different binding modes among the carbonyl oxygen of the PDI and the K^+ cations localized at the channel walls. Color codes as in Fig. 2 of the main text.

References

- 1) G. Tabacchi, E. Fois, G. Calzaferri, *Angew. Chem. Int. Ed.* 2015, **54**, 11112.
- 2) J. M. Newsam, *J. Phys. Chem.* 1989, **93**, 7689-7694
- 3) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868.
- 4) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892-7895.
- 5) N. Troullier, J. L. Martins, *Phys. Rev. B* 1991, **43**, 1993.
- 6) R. Car, M. Parrinello, *Phys. Rev. Lett.* 1985, **55**, 2471.
- 7) A. Laio, M. Parrinello, *Proc. Natl. Acad. Sci. USA* 2002, **99**, 12562.
- 8) CPMD code, MPI für Festkörperforschung: Stuttgart, Germany; IBM Zürich Research Laboratory: Zürich, Switzerland, **1990–2012**, www.cpmd.org