On the molecular mechanisms for the H_2/CO_2 separation performance of zeolite imidazolate framework two-layered membranes

Electronic Supporting Information

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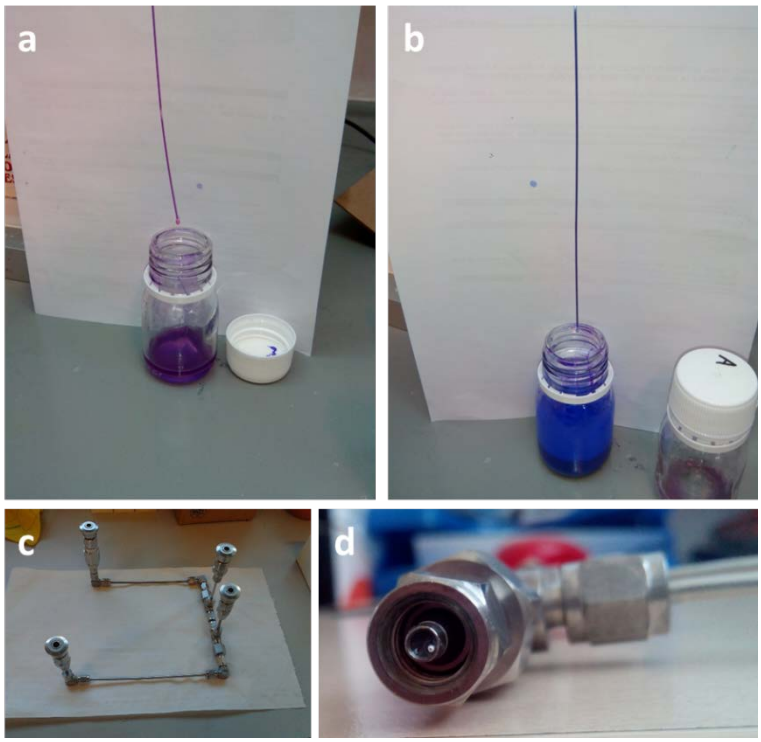

Figure S1. Images of the microfluidic ZIF@P84 HF membrane synthesis, showing ZIF-9 liquid phase epitaxy (LPE) steps: support wetting with the cobalt salt purple solution (a) and pumping of deprotonated ligand giving rise to crystalline blue ZIF-9 (b). HF gas permeation module for HF membrane testing (c) and higher magnification showing the epoxy resin sealing (d).

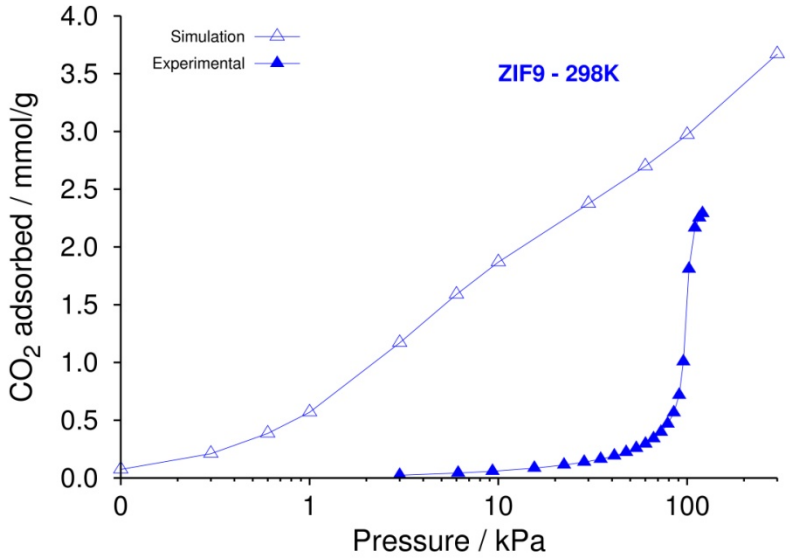

Figure S2. Simulated (empty) and experimental (filled symbols) ZIF-9 CO_2 adsorption isotherm at 25 ºC. Phase transitions upon loading that cannot yet be reproduced by molecular simulation are clearly shown in the experimental curve.

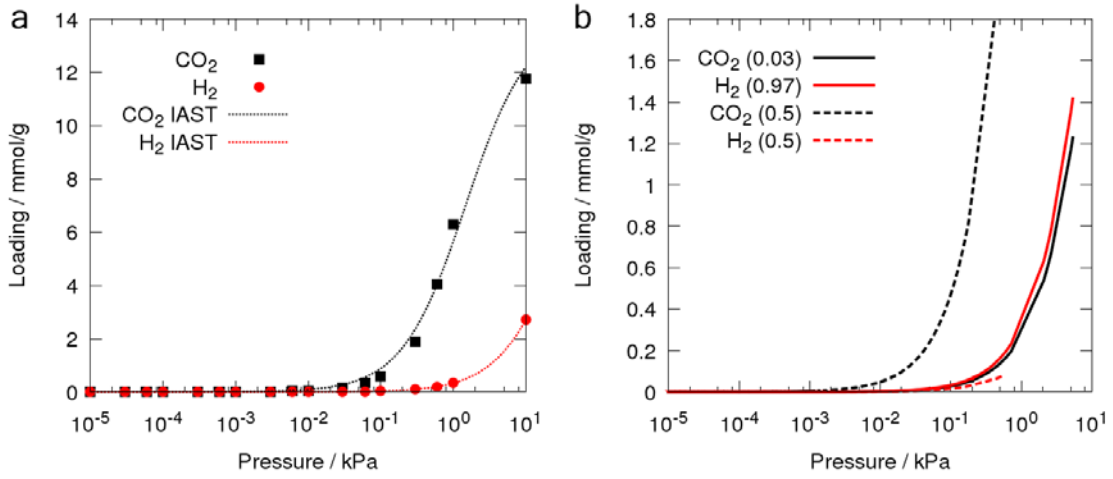

Figure S3. (a) Pure CO_2 and H_2 simulated adsorption isotherms in ZIF-8 at 35 ºC (symbols) and their respective IAST adjustments (dotted lines). (b) 97% H_2 / 3% CO_2 mixture (continuous lines) and equimolar H_2/CO_2 mixture (dashed lines) predicted adsorption isotherms by IAST in ZIF-8 at 35 ºC (see further information on IAST below).

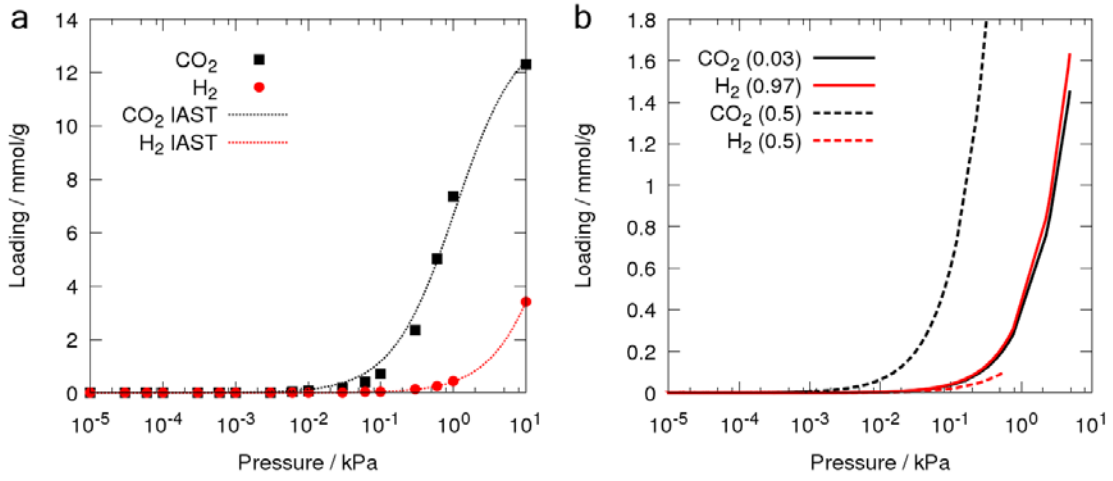

Figure S4. (a) Pure CO_2 and H_2 simulated adsorption isotherms in ZIF-67 at 35 ºC (symbols) and their respective IAST adjustments (dotted lines). (b) 97% H_2 / 3% CO_2 mixture (continuous lines) and equimolar H_2/CO_2 mixture (dashed lines) predicted adsorption isotherms by IAST in ZIF-67 at 35 ºC (see further information on IAST below).

The Ideal Adsorption Solution Theory (IAST)[S1] is an approach to make predictions of adsorption isotherms for fluid mixtures from the pure-component data, which are easier to obtain both in experimental and computational ways. The approach has been widely used to accurately describe light gas mixture adsorption isotherms, e.g. CO_2 and H_2, in several porous materials, including ZIFs. Prior to making the mixture prediction, it is necessary to fit the model used to describe the behaviour of the pure compounds in the adsorbents (left plots in Figures S3 and S4), and then, using the same model, to carry out the mixture calculations (right plots in Figures S3 and S4). For our systems, Langmuir model[S2] was used.

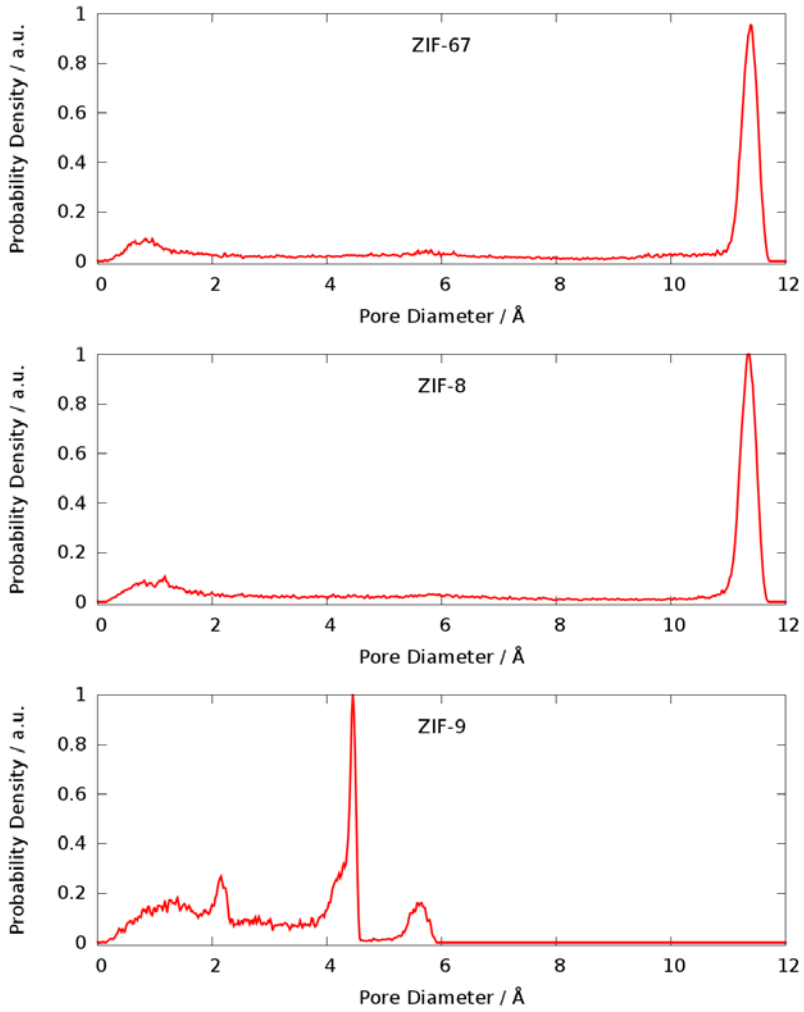

Figure S5. Pore size distribution (PSD) of ZIF-67, ZIF-8 and ZIF-9 materials obtained by molecular simulation using the method reported by Gelb and Gubbins.[S3]

Table S1. Large Cavity Diameter (LCD) and Pore Limiting Diameter (PLD) of ZIF-67, ZIF-8 and ZIF-9 materials obtained by using Zeo++ program.[S4-S5]

Material	LCD / Å	PLD / Å
ZIF-67	11.84	3.43
ZIF-8	11.81	3.46
ZIF-9	5.62	2.44

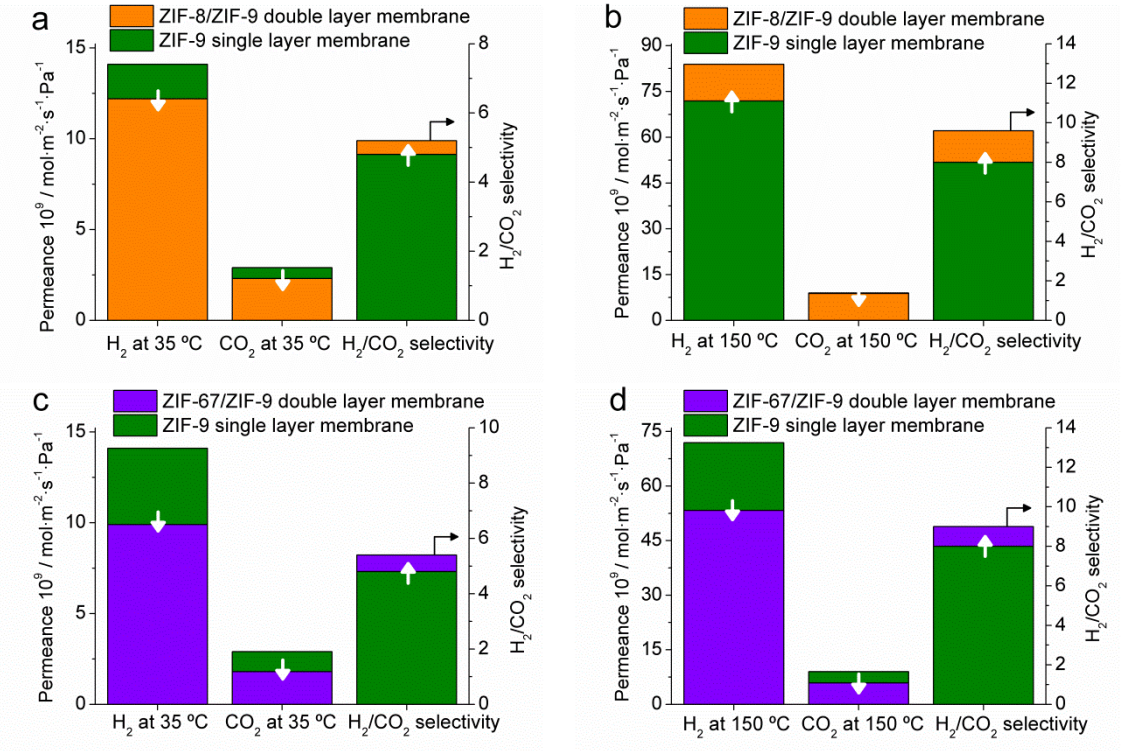

Figure S6. H_2 and CO_2 permeances and H_2/CO_2 selectivity comparison between single ZIF-9 and double-layered ZIF-8/ZIF-9 (a,b) and ZIF-67/ZIF-9@P84 (c,d) membranes at two different temperatures (35 and 150 ºC). White arrows indicate the variations after the mIm-based ZIF (ZIF-8 or ZIF-67) layer growth on ZIF-9.

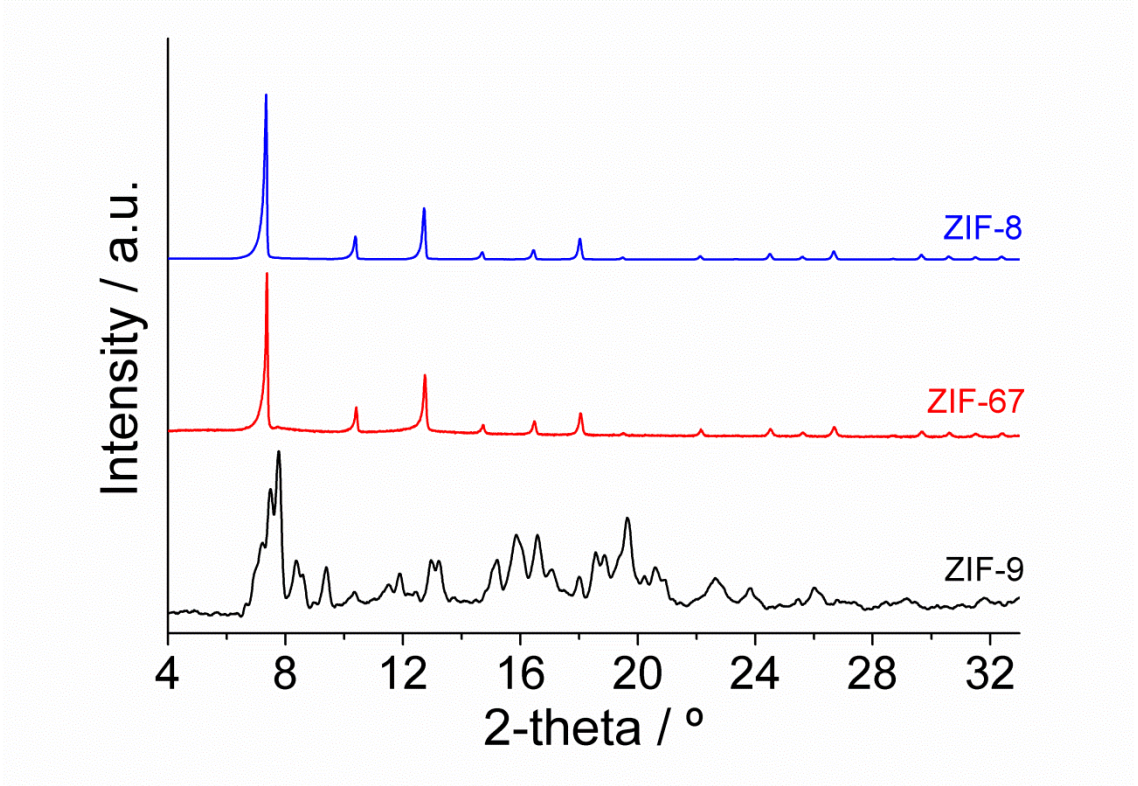

Figure S7. XRD spectra of the powdered ZIF materials after a 24 h-treatment at 175 ºC, similar to the conditions of the gas separation tests carried out. As observed when compared with Figure 4, the materials retain their crystalline structures.

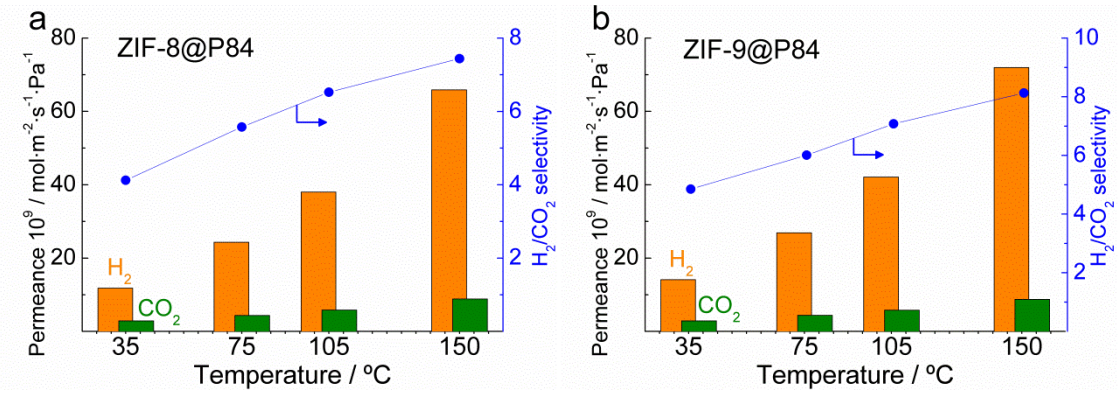

Figure S8. Single-layered ZIF-8 (a) and ZIF-9 (b) membrane permeation properties in the H_2/CO_2 mixture separation depending on the temperature in the 35-150 ºC range. Apparent activation energies were calculated and shown in Table 2.

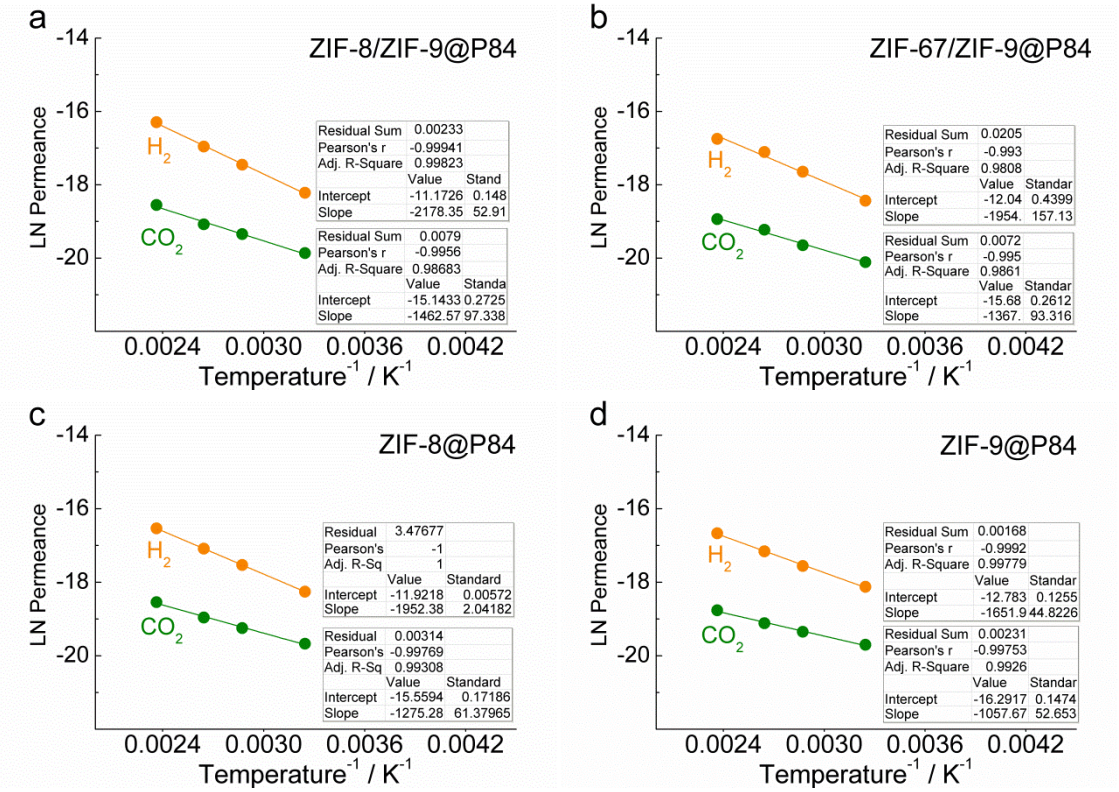

Figure S9. H_2 and CO_2 permeance fittings to the Arrhenius equation in the 35-150 ºC range resulting in the apparent activation energies E_a shown in Table 2 for the ZIF-8/ZIF-9 (a) and ZIF-67/ZIF-9 (b) double-layered and the ZIF-8 (c) and ZIF-9@P84 (d) single-layered HF membranes.

Table S2. H_2/CO_2 separation performance of MOF-supported hollow fiber membranes in the literature.

Ref.	MOF	HF support	T [°C]	H_2 permeance [GPU]	α H_2/CO_2
S6	ZIF-90	Torlon®	35	580	1.8*
S7	ZIF-7	PVDF	Room	7031	18.4*
S7	ZIF-8	PVDF	Room	6016	16.3*
S8	ZIF-8	PVDF	Room	5684	12.4
S8	ZIF-7	PVDF	Room	3053	15.9
S9	ZIF-8	PVDF	-	60000	7.0*
S10	HKUST-1	PVDF	25	5884	8.1
S11	HKUST-1	PSf / PMDS	Room	1449	21.0*
S12	HKUST-1	PAN	20	210448	7.1
S8	HKUST-1	PVDF	Room	17957	7.9
S13	NH_2-MIL-53	PVDF	Room	16179* / 12576	30.4* / 32.3
This work	ZIF-8/ZIF-9	P84®	150	250	9.6
This work	ZIF-67/ZIF-9	P84®	150	159	9.0

*Ideal selectivies.

Supporting Information References

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