Molecular Recognition-Induced Structural Flexibility in ZIF-71

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SUPPORTING INFORMATION

FIGURES

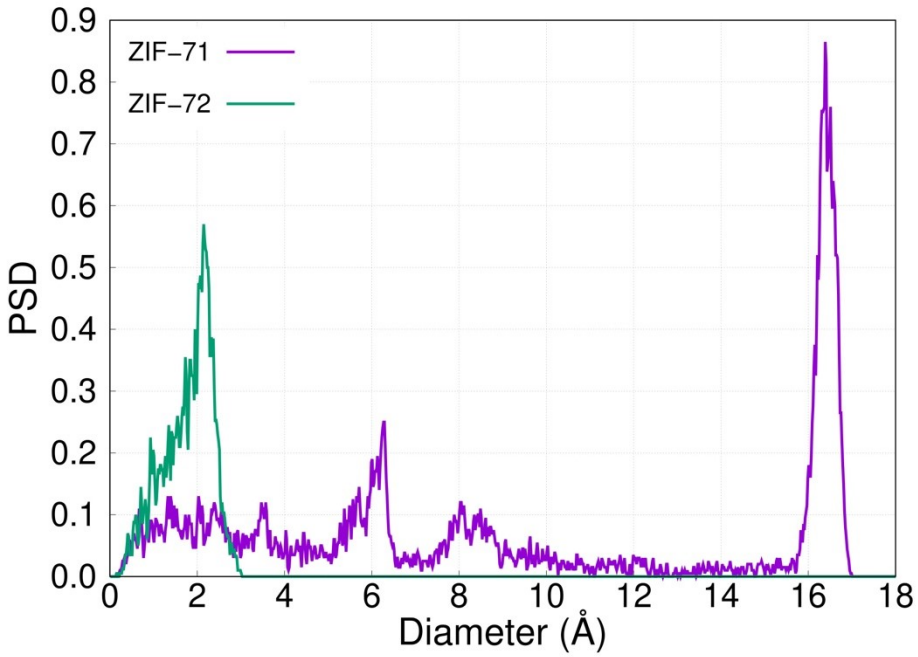


Figure S1. Simulated pore size distribution (PSD) for ZIF-71 and ZIF-72.

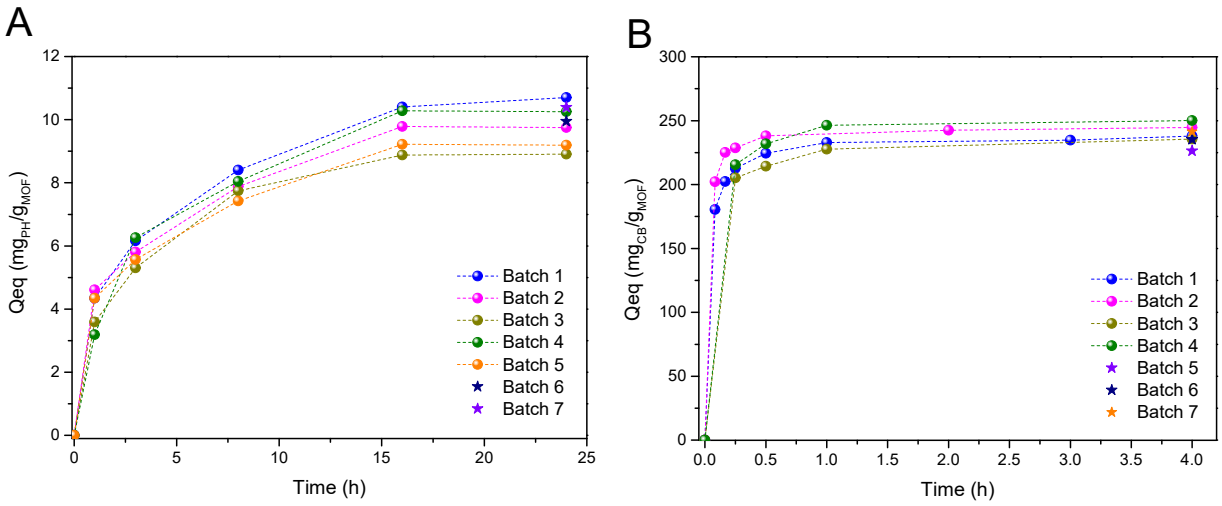


Figure S2. Adsorption kinetic studies for (A) phenol and (B) chlorobenzene at 298 K in ZIF-71 sample.

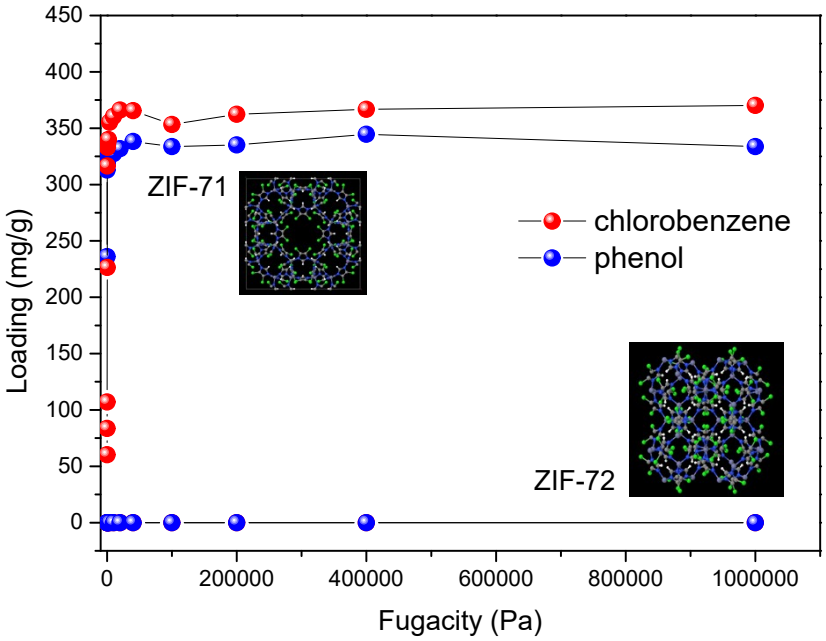


Figure S3. Simulated adsorption isotherms for phenol and chlorobenzene in ZIF-71 and ZIF-72.

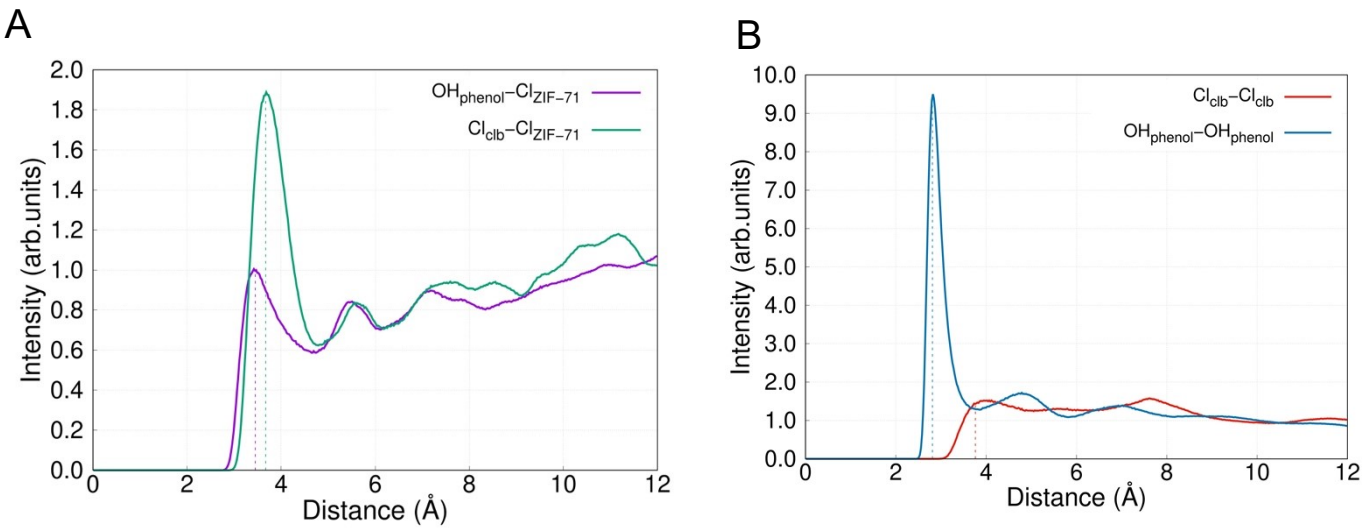


Figure S4. A Amplification of the OH and Cl distances in the two probes evaluated with the Cl groups in the ZIF-71 linker, and **B** Amplification of the intermolecular distances in equilibrium upon adsorption in ZIF-71.

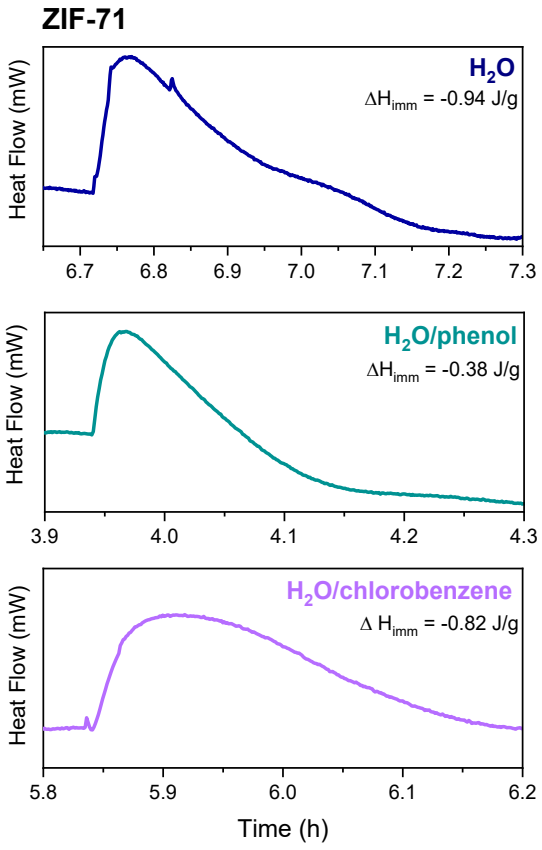


Figure S5. Immersion calorimetry measurements of ZIF-71 into (A) water, (B) a phenol/water solution, and (C) a chlorobenzene/water solution.

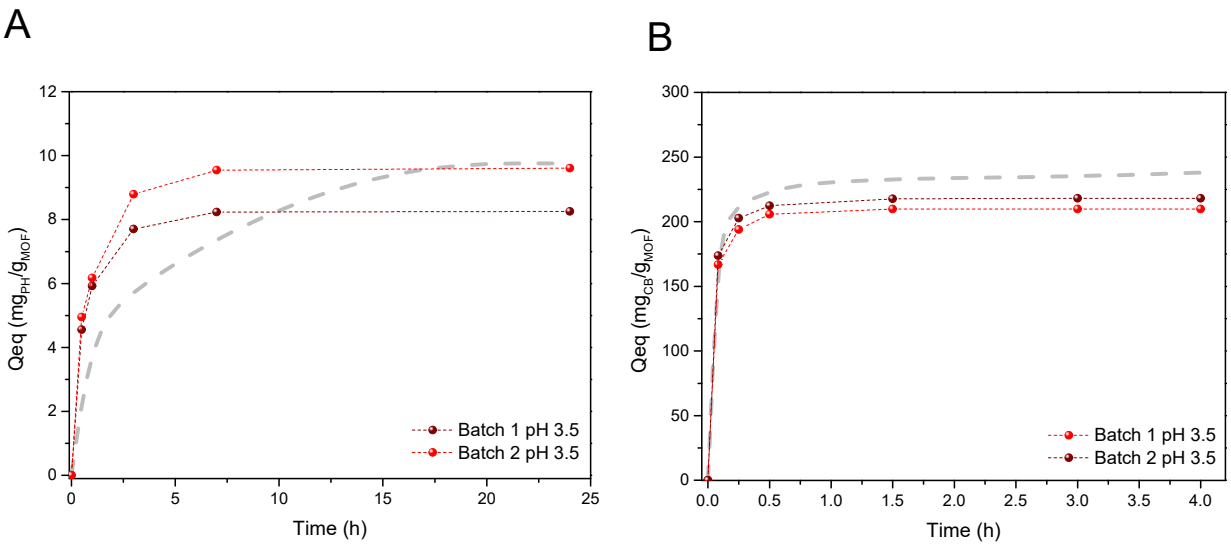


Figure S6. Adsorption kinetic studies for (A) phenol and (B) chlorobenzene at 298 K in ZIF-71 sample under acidic conditions (pH 3.5 adjusted using a HCl solution). Average adsorption kinetics (data from Figure S2), obtained under non-modified pH conditions, have been added as a grey slashed line for the sake of comparison.

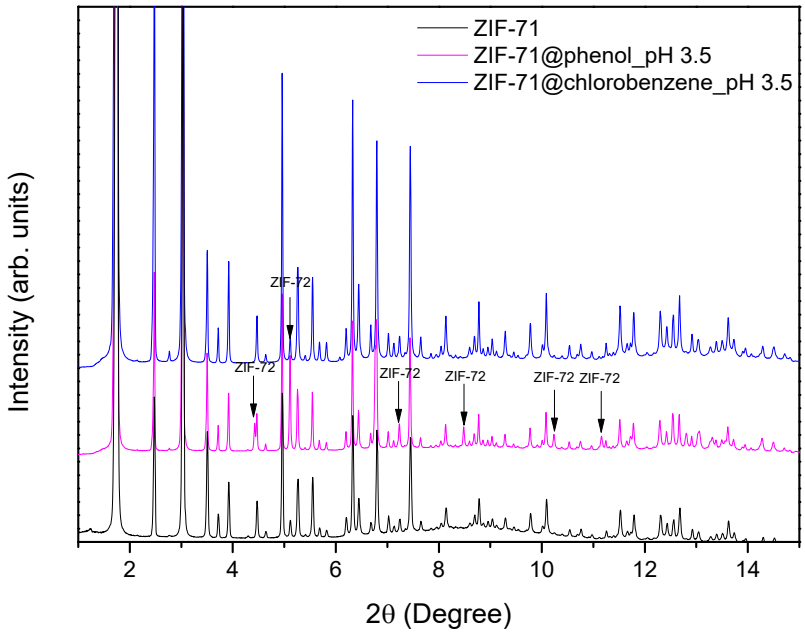


Figure S7. Synchrotron X-ray powder diffraction patterns of ZIF-71 before and after the chlorobenzene and phenol adsorption tests under acidic conditions (beam energy 20 keV).

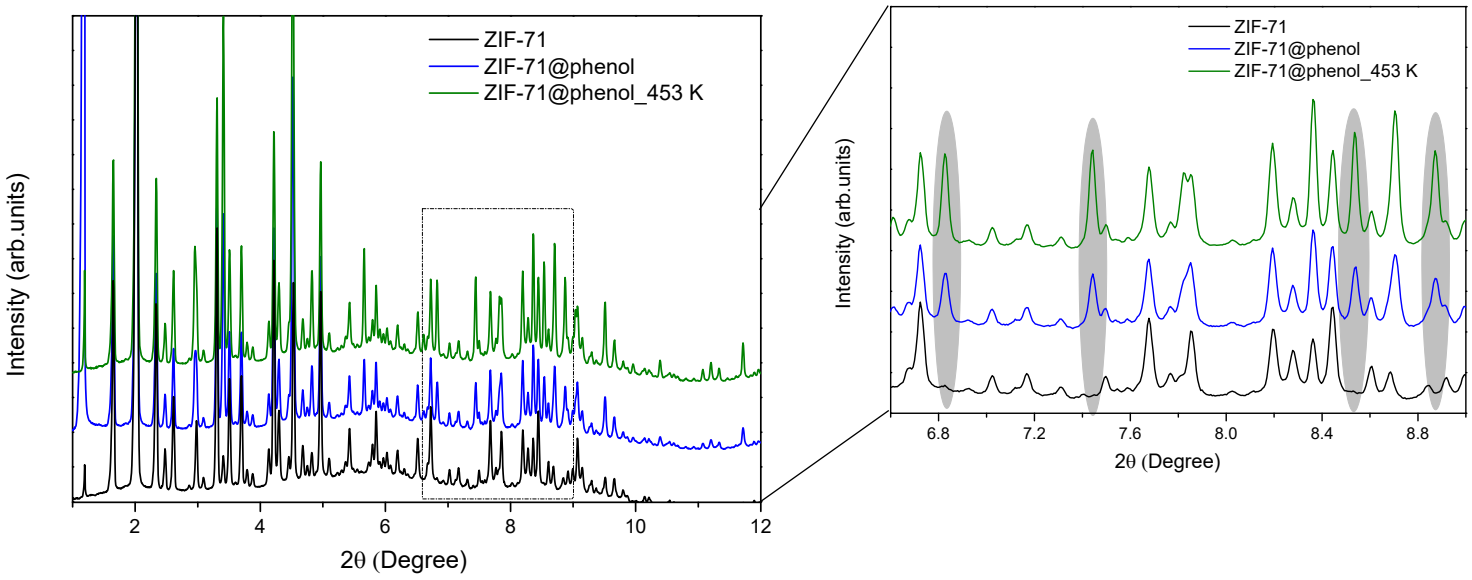


Figure S8. Synchrotron X-ray powder diffraction patterns of ZIF-71 before and after the phenol adsorption tests (beam energy 30 keV). The used sample was submitted to a thermal treatment at 453 K to promote the phase transition. Low 2 Theta peaks in ZIF-71@phenol (ca. 1.2°) correspond to entrapped water.

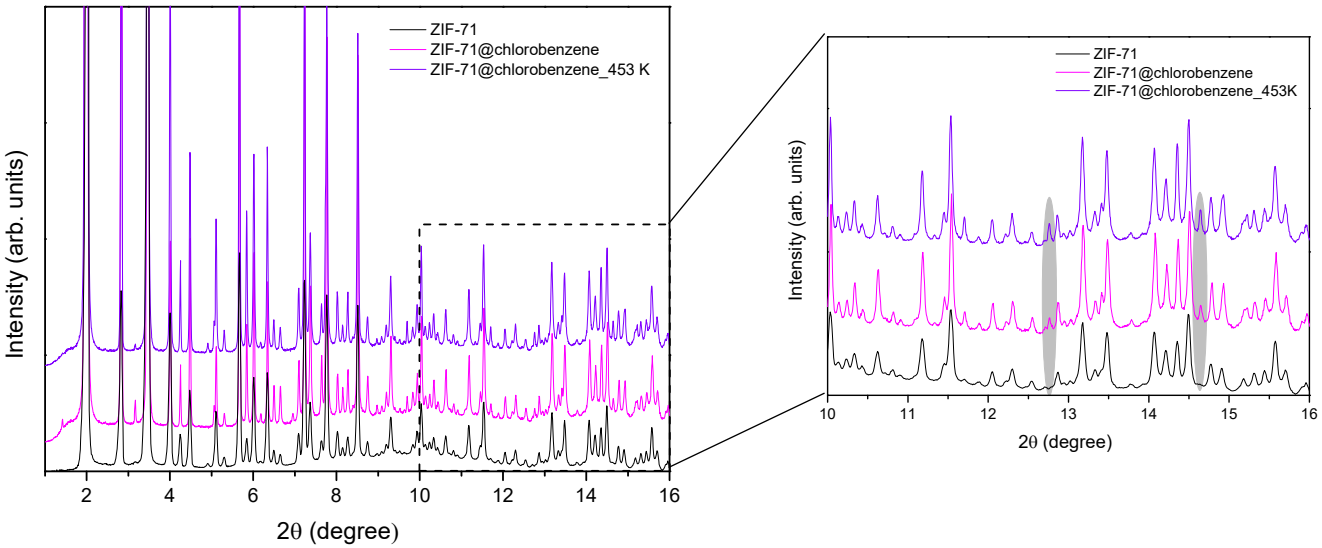


Figure S9. Synchrotron X-ray powder diffraction patterns of ZIF-71 before and after the chlorobenzene adsorption tests (beam energy 17.5 keV). The used sample was submitted to a thermal treatment at 453 K to promote the phase transition.

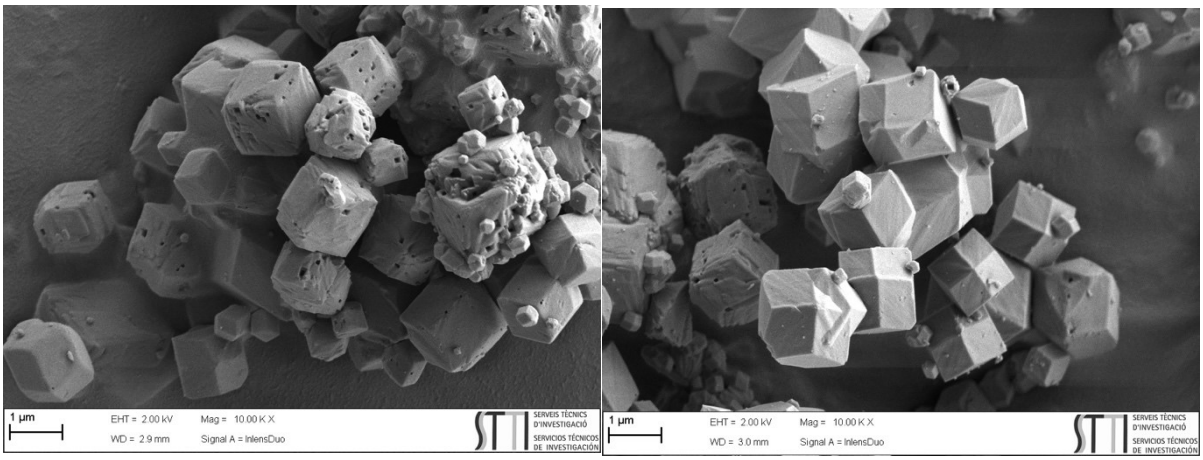


Figure S10. Representative FESEM images of ZIF-71 after the phenol adsorption process, a subsequent drying and a heat treatment at 453 K.

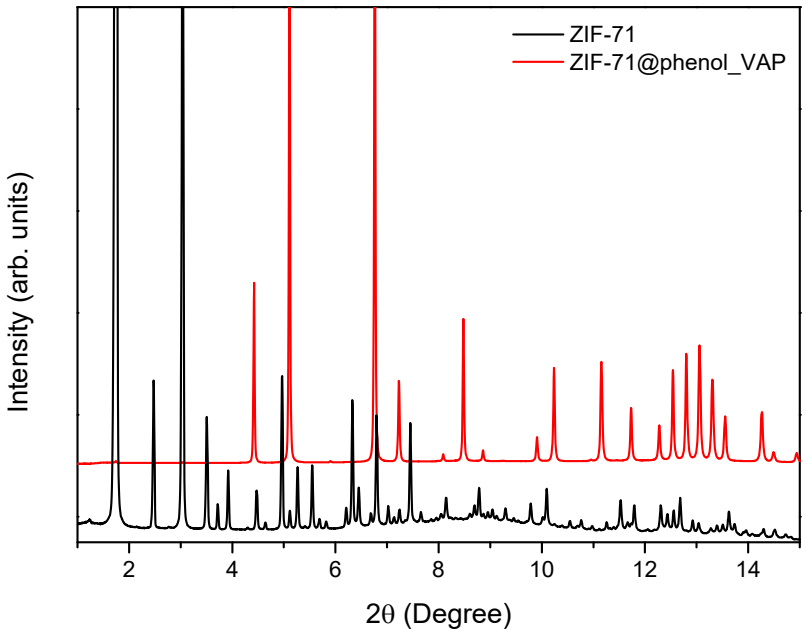
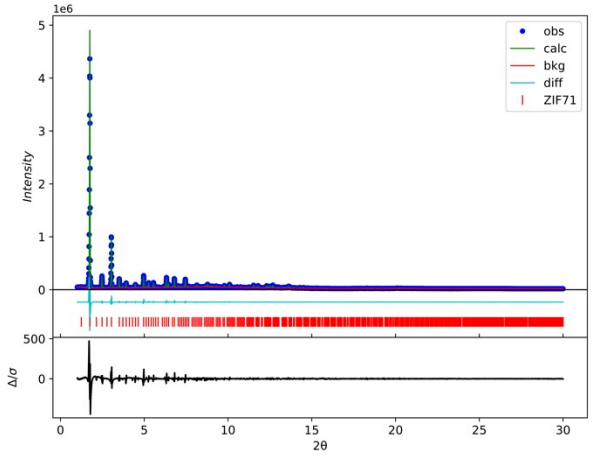
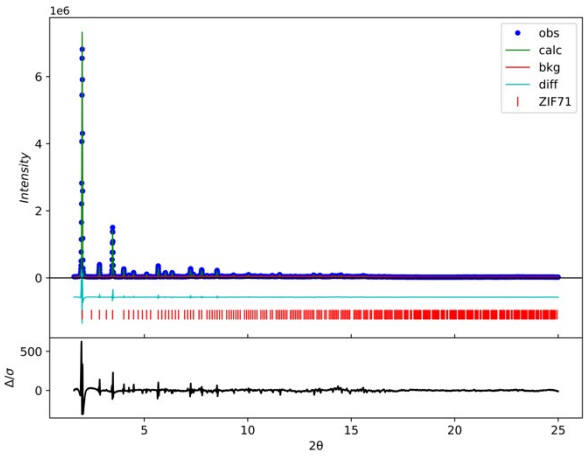


Figure S11. Synchrotron X-ray powder diffraction patterns of ZIF-71 before and after exposure to the vapors of an aqueous solution of phenol (50 ppm) (beam energy 20 keV).

Dry ZIF-71



ZIF-71@H_2O



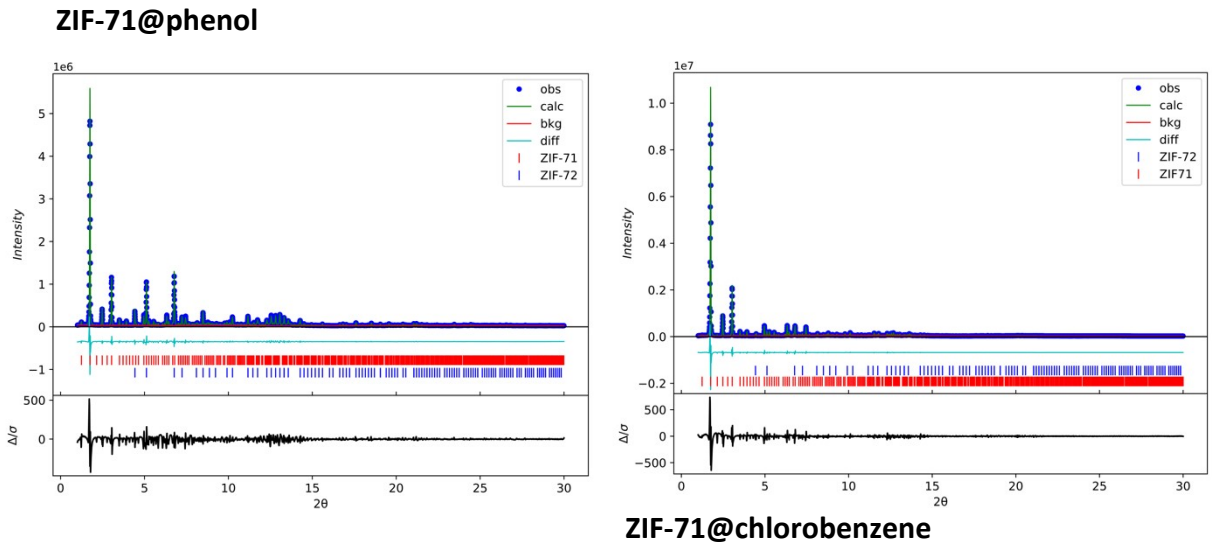


Figure S12. Rietveld refinement of the different SXRPD patterns obtained.

TABLES

Table S1: Lennard-Jones parameters and partial charges of the atoms from the structures. Different types of atoms were defined for a given element according to their chemical environment. The proposed labelling of atoms is shown below.

Atom Type	**ε/k_B (K)**	**σ (Å)**	**charge (e^-)**
Zn1	62.40	2.462	0.7

C1	52.84	3.431	0.0371
H1	22.14	2.571	0.049
N2	34.72	3.261	-0.19355
C3	52.84	3.431	0.0189
Cl4	114.23	3.517	-0.0434

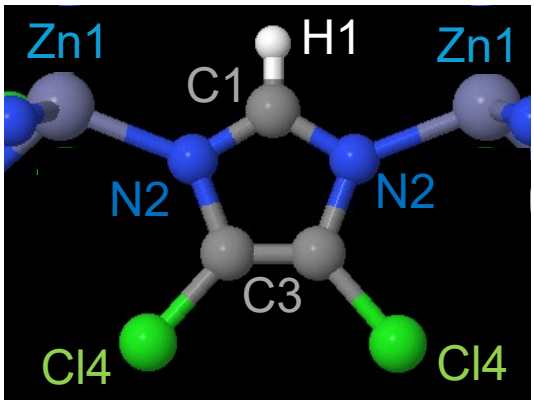


Table S2. Henry coefficients and Heat of adsorption for the three probes evaluated obtained from the GCMC simulations.

Henry Coefficient (ml/kg/Pa)					
ZIF-71			ZIF-72		
phenol	chlorobenzene	water	phenol	chlorobenzene	water
1.10 ± 0.01	0.135 ± 0.001	$1.1 \cdot 10^{-6} \pm 9.6 \cdot 10^{-9}$	$1.0 \cdot 10^{-95} \pm 4 \cdot 10^{-95}$	$1.1 \cdot 10^{-142} \pm 4.6 \cdot 10^{-142}$	$1.2 \cdot 10^{-9} \pm 2 \cdot 10^{-11}$

Heat of Adsorption (kJ/mol)					
ZIF-71			ZIF-72		
phenol	chlorobenzene	water	phenol	chlorobenzene	water
-66.63 ± 0.11	-61.49 ± 0.70	-13.89 ± 0.10	491 ± 30	780 ± 57	-6.72 ± 0.06

Table S3: Structural parameters calculated for ZIF-71 before (pristine) and after being applied in the phenol and chlorobenzene adsorption process. The amount of ZIF-72 determined from the Rietveld refinement is included for each specific case.

Sample	ZIF-71		ZIF-72	
	a, Å	wt.%%	a, Å	wt.%%
ZIF-71 dry	28.6387	100%	Not observed	
ZIF-71@phenol	28.6428	46.5	19.6513	53.5
ZIF-71@chlorobenzene	28.6304	100%	Not observed	