

Supporting Information for:

**Polychlorinated Aromatics Adsorption in EMT-
Type Zeolite: a Combined Experimental-
Simulation Approach**

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S1. EMT-type zeolite structure and its cationic distribution

EMC-2 zeolite, also known as hexagonal faujasite or Breck's structure Six, is a faujasite-like, large pore zeolite, first synthesized in pure phase by Delprato *et al.*¹, using crown-ether based molecules as structure directing agents. Numerous synthetic zeolites (ZSM-3, ZSM-20², CSZ-1, ECR-30) correspond to inter-grown materials where sheets of hexagonal (EMT) and cubic (FAU) structures are stacked in various manners³. Both, FAU and EMT frameworks are built on the basis of identical composite building units: double six rings (D6R, also called hexagonal prisms) and sodalite cages (also called β cage). Further, in both frameworks each sodalite cage is interconnected *via* a hexagonal prism to 4 other sodalite cages, creating a tetrahedral configuration. The difference between FAU and EMT topologies can be described on different levels. First, whereas in FAU structure the symmetry operation involved in the connection of the sodalite cages through the hexagonal prisms is an inversion center, in the EMT topology, for one of the four hexagonal prisms the connection occurs via a mirror plane⁴. Further, the planes formed by a honeycomb arrangement of sodalite cages interconnected through D6R are stacked in a hexagonal fashion in EMT, and in cubic way in FAU⁵. Finally, as a consequence of cubic stacking in the FAU-type zeolite there is a unique type of "supercage" (~13 Å of diameter), whereas a hexagonal stacking initiates two types of supercages in its structure: smaller ones, the as-called "hypocages", delimited through three twelve-membered rings (12-MR) and larger ones, designed as "hypercages", delimited by five 12-MR. The EMT framework with highlighted hypo- and hypercages is represented in Figure S1⁶.

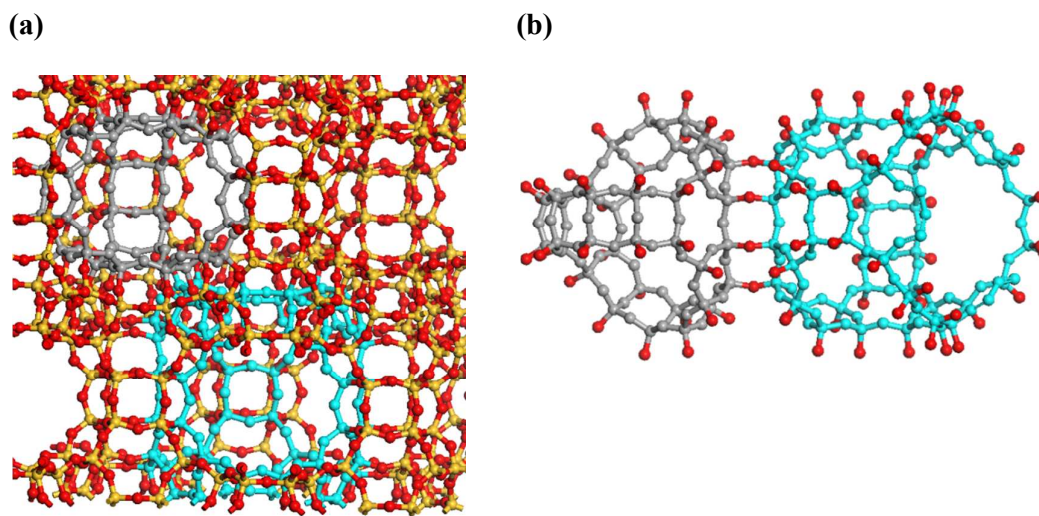


Fig.S1. (a) EMT-type zeolite framework with hypocage highlighted in silver and hypercage in cyan. (b) A detailed view on hypocage (in silver), connected to the hypercage (in cyan).

The EMT-type zeolite exists in the aluminosilicate form ($\text{Si}:\text{Al} = 3.8$) with Na^+ as charge compensating cations. The crystallographic sites hosting Na^+ cations are labeled analogously to the Y Faujasite structure⁷: site I within the hexagonal prism, site I' inside the sodalite cage, in front of the hexagonal prism six-membered ring and site II close to the sodalite cage 6-membered ring inside the supercage. Note that no population of crystallographic sites III and III' has been observed, according to the relatively high Si/Al molar ratio of the EMC-2 zeolite framework. Indeed, sites III and III' are occupied only at high aluminum content corresponding to a Si/Al molar ratio lower than 1.5. In EMT-type zeolite, one additionally distinguishes two kinds of cationic sites: (1) situated within the part of the structure with the inversion center containing hexagonal prisms

(sites labeled “a”) and (2) situated within the part of the structure with the hexagonal prisms containing the mirror plane (sites labeled “b”). Thus, six different cationic crystallographic sites can be distinguished within the aluminosilicate EMC-2 zeolite with Si/Al molar ratio of 3.8: Ia, Ib, I’a, I’b, IIa and IIb.

S2. EMT-type zeolite synthesis

S2.1 REACTANTS AND PROBE MOLECULES

Sodium hydroxide (99.99 wt %, Riedel de Haën), colloidal silica (Ludox AS-40, Aldrich), sodium aluminate (57 wt % Al_2O_3 , 40 wt % Na_2O , Strem Chemicals), 18-crown-6 (95 wt %, Alfa Aesar) and deionized water were chemical reagents. Anhydrous ortho- (*o*-DCIB) and meta-dichlorobenzenes (*m*-DCIB) were purchased from Sigma-Aldrich, and further used as received.

S2.2 MATERIALS SYNTHESIS

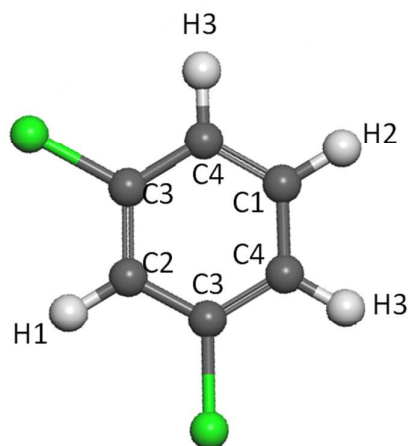
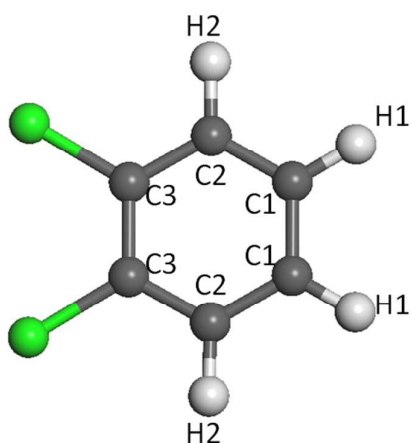
For the EMC-2 zeolite synthesis, a gel with the following molar composition 2.1 Na_2O : 10 SiO_2 : 1 Al_2O_3 : 0,5 18-crown-6: 100 H_2O was placed in a PTFE-lined stainless steel autoclave and heated at 110 °C in static conditions for 19 days¹. After the synthesis, the suspension is filtered and the precipitate is rinsed abundantly with distilled water 3 times, and dried at 70 °C. In order to remove the organic template occluded in the zeolite porosity, the as-synthesized sample is calcined under air during 4h at 550 °C with a heating rate of 1°. min^{-1} .

S3. Force field parameters

Table S1. Lennard-Jones parameters (ϵ/k_B , σ) and partial atomic charges (q) carried by adsorbate and adsorbent atoms. The scheme gives the denomination of adsorbate molecules constituting atoms. The parameters have been extracted from the Clay force field for zeolites⁸ and from the TraPPE force field for adsorbates⁹. Green, black and white balls correspond to Cl, H and C atoms, respectively.

Parameters for the non-bonded interactions			
Atom	ϵ/k_B (K)	σ (Å)	$q(e)$
C(1)(o-dichlorobenzene)	30.70	3.60	-0.11
C(2)(o-dichlorobenzene)	30.70	3.60	-0.08
C(3)(o-dichlorobenzene)	30.70	3.60	0.08
H(1)(o-dichlorobenzene)	25.45	2.36	0.11
H(2)(o-dichlorobenzene)	25.45	2.36	0.10
Cl(o-dichlorobenzene)	149	3.42	-0.1
C(1)(m-dichlorobenzene)	30.70	3.60	-0.14
C(2)(m-dichlorobenzene)	30.70	3.60	0.00
C(3)(m-dichlorobenzene)	30.70	3.60	0.03
C(4)(m-dichlorobenzene)	30.70	3.60	-0.05
H(1)(m-dichlorobenzene)	25.45	2.36	0.08
H(2)(m-dichlorobenzene)	25.45	2.36	0.12
H(3)(m-dichlorobenzene)	25.45	2.36	0.10

Cl(<i>m</i>-dichlorobenzene)	149	3.42	-0.11
O (zeolite)	78.20	3.17	-1.20
Si (zeolite)	0.93E-3	3.30	2.40
Al (zeolite)	0.93E-3	3.30	1.40
Na⁺ (zeolite)	65.47	2.35	1.00



S4. Parameters of the zeolite structures optimized on the DFT level

Table S2. Comparison between the DFT fully relaxed simulated cell parameters of the EMT-type zeolite (P1 symmetry) in the purely siliceous (EMT (SiO₂) and aluminosilicate (Na-EMT) forms in the absence (empty) and in the presence of the *o*- and *m*-DCIBs adsorbates.

Structure	Empty	EMT(SiO ₂)	EMT(SiO ₂)	Empty	Na-EMT	Na-EMT
	EMT	+	+	EMT	+	+
Cell	(SiO ₂)	<i>o</i> -DCIB	<i>m</i> -DCIB	(Na-EMT)	<i>o</i> -DCIB	<i>m</i> -DCIB

parameters						
a (Å)	17.081	16.996	16.996	16.975	16.937	16.941
b (Å)	17.081	16.996	16.997	16.996	16.935	16.942
c (Å)	27.689	27.403	27.412	27.998	27.967	27.9615
α (°)	90.002	89.942	90.011	90.03	90.102	90.133
β (°)	90.007	90.073	89.992	90.37	90.174	90.201
γ (°)	120.038	120.053	120.072	120.59	120.440	120.444
V (Å ³)	6993.350	6851.488	6852.975	6953.39	6915.68	6918.77

S5. Adsorption energies extracted from the DFT calculation

Table S3. Adsorption Energies (given in kJ/mol) obtained by the DFT-D2 calculations for the *o*- and *m*-DCIBs adsorbed within purely siliceous ((EMT(SiO₂)) and aluminosilicate (Na-EMT) EMT-type materials

DCIB		
	Ortho-	Meta-
Zeolite		
EMT (SiO ₂)	-66.2	-68.6
Na-EMT	-132.8	-122.1

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