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"We adore chaos because we love to produce order": Inspired by the work of M. C. Escher, the image embodies the metamorphosis of a water–ethanol solution that is discussed by G. Tabacchi and co-workers in their Communication (DOI: 10.1002/anie.201610949). Chaotically distributed molecules are turned into a beautifully ordered two-dimensional pattern of dimers and tetramers. Order is produced at high pressure and through confinement in nanometric spaces (Illustration: Andrea Stangoni).

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Irreversible Conversion of a Water–Ethanol Solution into an Organized Two-Dimensional Network of Alternating Supramolecular Units in a Hydrophobic Zeolite under Pressure

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Abstract: Turning disorder into organization is a key issue in science. By X-Ray Powder Diffraction and modeling studies, here we show that high-pressure and the shape-space constraints of the hydrophobic all-silica zeolite ferrierite separate an ethanol-water liquid mixture into ethanol dimer wires and water square tetramers. The confined supramolecular blocks alternate each other in a binary two-dimensional (2D) architecture, that remains stable upon complete release of pressure. These results support the combined use of high pressures and void space networks as a viable strategy for driving the organization of molecules or nano-objects towards complex, pre-defined patterns relevant for the realization of novel functional nanocomposites.

Supramolecular organization induced by external stimuli has opened new paths for the bottom-up fabrication of nanostructures.[1] Under a stimulus – light, chemicals, electric fields, or magnetic forces – molecules or nanospecies can form patterns in solution and on suitable supports, leading to cooperative effects and materials with new properties.[2] This idea has given momentum to the quest of organized systems in nanoporous containers like zeolites.[3] The realization of nanoladders of dyes in Zeolite L – a porous host with a one-dimensional channel system – illustrates how zeolites can shape their molecular content: confinement, combined with a high dye-loading increase (the "external stimulus"), ensured spatial and morphologic control over the self-assembly process of the dye molecules.[3e] Channel systems in two perpendicular directions would greatly enhance the number and variety of attainable supramolecular architectures.[4] Yet this route is scarcely pursued because the organization of molecular species in two dimensions is more difficult to control,[5] and progress would require fundamental issues to be tackled.[4] One of these is whether structural complexity could arise from disorder.[1] Here we show that inherently disordered systems such as binary liquid mixtures can be irreversibly converted by pressure in organized 2D-architectures where the distribution of the molecular components is tailored by the zeolite pores.

Since long time water is known to form supramolecular structures, like one-dimensional ice[6a-e] or water triple helix,[6f,g] when confined in convenient zeolite materials; notably, some of them are also stable at high pressure conditions.[7] Moreover, water can be incorporated in both hydrophilic and hydrophobic zeolites by using water mixtures as pressure transmitting media (PTM).[8] Mostly adopted are methanol, ethanol and water (m.e.w) mixtures in (16:3:1) proportion, which allow to reach pressures up to about 9 GPa in Diamond Anvil Cells (DAC).[9] At such conditions, only water enters the two-dimensional (2D) channel system of the hydrophobic all-silica zeolite ferrierite [$Si_{36}O_{72}$] (Si-FER),[10] forming stable aggregates.[11] This suggest that pressure might enhance the shape-directing action of the zeolite matrix, triggering the formation of organized arrangements of small molecules.

Herein we prove that combined effects of high pressures and shape constraints can separate strongly hydrogen-bonded liquid mixtures into their constituents and build structural complexity in two dimensions. An ethanol-water solution, injected *via* GPa pressure in Si-FER, turns into a regular 2D-network of ethanol dimers and water cyclic tetramers. Both components penetrate the zeolite cavities, but self-assemble in distinct regions. Most importantly, the organized segregation persists after pressure release, and the pressure-created supramolecular artwork is stable at room conditions as well.

To try inserting both ethanol and water in Si-FER, instead of m.e.w. we adopted a mixture of (1:3) ethanol and water (e.w.) as PTM,[8e] in the 0.20÷1.34 GPa range. The system was analyzed *in situ* by high-pressure synchrotron X-ray powder diffraction (XRPD) and refined via first principles modeling.

The diffraction data indicate the insertion of molecular species into the initially empty zeolite. Figure 1 - featuring selected powder patterns of Si-FER in e.w. - shows that the intensity ratio among the low-theta peaks, which is sensitive to the extraframework content, is affected by an evident variation. This is a clear indication that molecules enter Si-FER also at relatively low pressures.[12] The appearance of very weak peaks at 1.04 GPa indicates a phase transition from the orthorhombic *Pmnn* to the monoclinic $P2_1/n$ space group. No amorphization is observed in the explored pressure range, and, remarkably, all features of the patterns collected at low pressure, but the peak intensity ratios, are reversibly recovered upon complete release of pressure. The chosen zeolite is thus suitable for pressure-driven encapsulation of molecular species.

The elastic behavior (Figure 2) indicates that the most compressible parameter is *b* (Δb = -1.3%), while *a* and *c* are more rigid (Δa = -0.8%; Δc = -0.9%). These variations account

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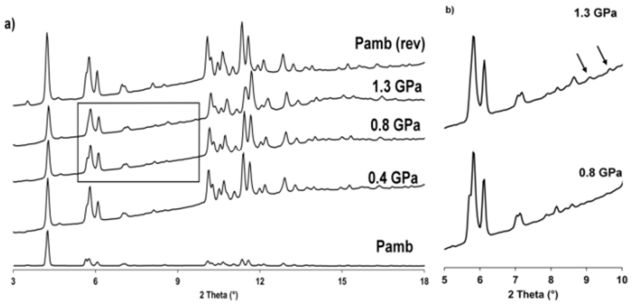


Figure 1. a) Selected integrated powder patterns, reported as a function of pressure. The P_{amb} pattern was collected in capillary; the P_{amb}(rev) upon decompression in DAC. b) magnification of the box in Figure 1a showing the transition from orthorhombic to monoclinic symmetry.

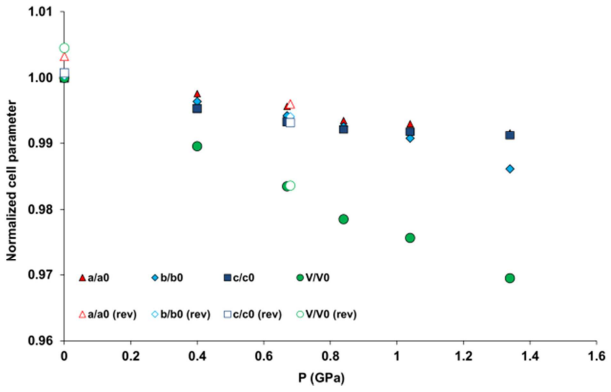


Figure 2. Si-FER lattice parameters as a function of pressure.

for a total volume decrease of 3% in the P_{amb} ÷ 1.34 GPa range. Importantly, the patterns collected upon decompression (labeled (rev)) show a reversible behavior of the unit cell parameters, but not of the intensities. Such finding suggests that the intruded molecules remained inside Si-FER after removal of the external stimulus. This would imply irreversibility of the pressure-induced uptake and stability of the resulting structure at room conditions.

To identify the incorporated species, first we did a structure refinement at 0.84 GPa, *i.e.* before the phase transition. The refined structure (Table S2 and Figure S1 in SI) suggested the penetration of 4 ethanol (EtOH) and about 6-8 water molecules per unit cell. However, as the refinement was affected by high instability and provided unsatisfactory water distances (Table S3 in SI), we used the experimental data as a starting point for modeling[13] the Si-FER·(H_2O,EtOH) system at cell parameters corresponding to these pressure conditions. A proper description was obtained using a dispersion-corrected density functional approximation[14] and a theoretical scheme suitable for complex organic-inorganic systems[15] (Section 2 in SI). To establish the number of incorporated water molecules and their organization, we built Si-FER models containing 4 ethanol and *n* water molecules (*n*=6÷14) per unit cell, and determined the most stable one by DFT-based structural optimizations (SI, Section 2, Eq. 1-2). Comparison of the calculated relative stabilities (Figure 3a) indicates that the most stable structure (Figure 3b) contains 8 H_2O per Si-FER unit cell.

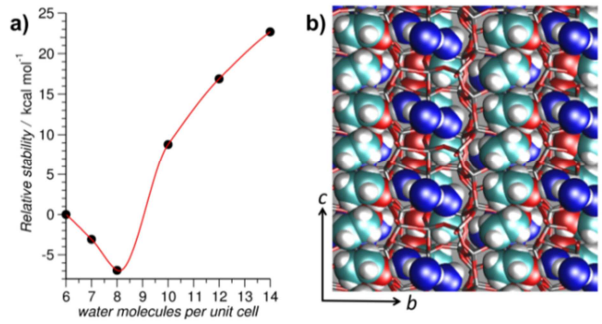


Figure 3. a) Relative stability (kcal mol^{-1}) of Si-FER·4EtOH·*n*H_2O models (n = 6,7,8,10,12,14). b) minimum energy structure of Si-FER·4EtOH·8H_2O projected in the *bc* plane. Si-FER (sticks): Si=grey; O=red. Guest molecules (spheres): EtOH: C=cyan, O=red, H=white; H_2O: O=blue, H=white.

The Si-FER framework features a 2D network of void space:[10] the 8-membered ring (8MR) channels along the *b* axis (Figure 4a) intersect two channel systems running in parallel along *c*, one with a larger diameter (10MR) and one smaller (6MR) (Figure 4b). Remarkably, water and ethanol are segregated in different channels (Figure 4c). While water occupies only the 6MR channels, EtOH is located in the 10MR ones - with the C-C bonds nearly perpendicular to the channel axis, thus forming wires of hydrogen bonded dimers (Figure 3b, Table 1). Some EtOH molecules also form weaker hydrogen bonds with Si-FER oxygens and water protons (Figure 4c). These results indicate that the applied pressure forced the organic portion of the mixture to self-organize in a quasi-1D structure, which interacts only weakly with the zeolite framework and the other component of the mixture, water. The organization of water is even more intriguing: it features groups of 4 molecules localized in the 6MR channels and arranged in a square via a closed chain of strong hydrogen bonds (Table 1, Figure 4c,d). Significantly, such water tetramers form no hydrogen bonds with the framework oxygens. This arrangement is stable also at room temperature, as shown by first principles molecular dynamics (SI, Table S4, Figures S3,S4), and persists even upon pressure release, as indicated by the data in Table 1. Notably, the hydrogen bond distances of the water tetramer show only tiny deviations from the minimum energy structure at 0.84 GPa. These findings can be explained by recalling that, while interactions with pore-walls (and with charge-balancing cations) are significant in hydrophilic zeolites, the behavior of water in hydrophobic systems is dominated by water–water hydrogen bonding, like in gas-phase water clusters.[16] Indeed, our square tetramer corresponds just to the most stable structure of 4 gas-phase water molecules.[17] The Si-FER models with *n*=6,10,12 H_2O also feature trimers, pentamers and hexamers of structure and connectivity corresponding to the most stable gas-phase $(H_2O)_n$ clusters (SI, Figures S5-S7).[17] Hence, the size and shape of Si-FER channels, perfectly tailored for very stable supramolecular units of the components, and the restricted void space at the channel intersections might lie at the origin of the segregation of water from ethanol in Si-FER.

Upon full pressure release, not only the zeolite keeps its molecular content unaltered in amount and organization, but it becomes slightly more stable (1.2 kcal mol^{-1}) compared to high-pressure conditions.

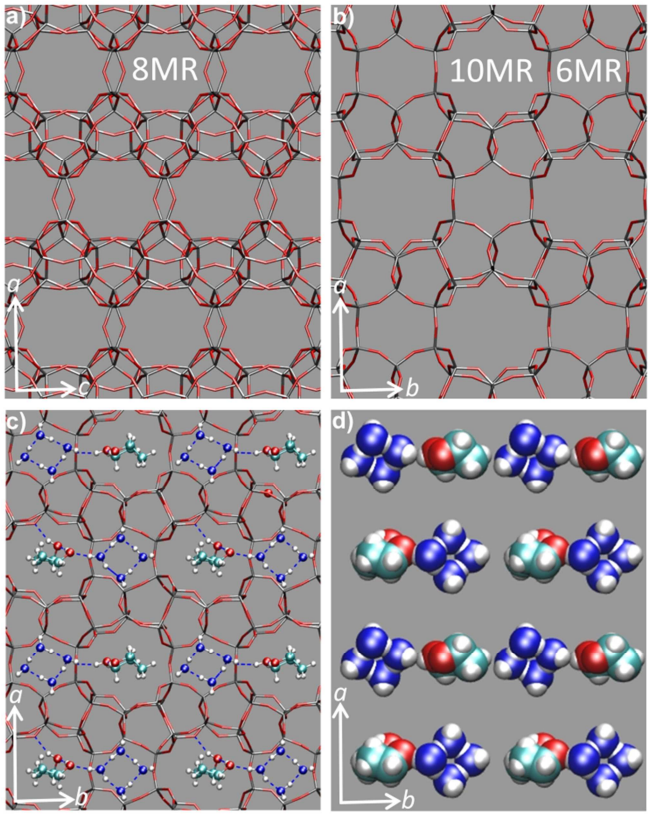


Figure 4. Optimized Si-FER framework (*P*=0.84 GPa) projected in: a) *ac* plane - showing the 8MR channels; b) *ab* plane - 10MR and 6MR channels, and organization in the Si-FER•4EtOH•8H_2O minimum structure at 0.84 GPa: c) hydrogen bond network (blue dotted lines). EtOH hydrogen bonds with framework oxygens and water protons: 1.994 Å and 1.795 Å, respectively; d) EtOH dimers and water tetramers.

Table 1. Hydrogen bond distances in Si-FER (Å)

H-bond [a]	0.84 GPa(i)	P_{amb}(rev)(i)	0.84 GPa(ii)	P_{amb}(rev)(ii)
[b]O_{E1}-H_{E2}	1.770	1.791	1.806	1.804
[c]O_{W1}-H_{W2}	1.713	1.711	1.774	1.778
[c]O_{W2}-H_{W3}	1.687	1.687	1.756	1.749
[c]O_{W1}-H_{W4}	1.691	1.694	1.595	1.609
[c]O_{W4}-H_{W1}	1.685	1.690	1.570	1.586

[a] The superscripts (i) and (ii) refer to the two distinct EtOH dimers/water tetramers in the Si-FER unit cell. [b] E1 and E2: the two EtOH in each dimer. [c] W1,2,3,4: the four H_2O in each tetramer.

Importantly, high pressure seems to be functional for irreversibility because complete filling of Si-FER with water is followed by extrusion when the maximum applied pressure is 0.3 GPa.[18] This suggests that the special water-ethanol arrangement and its stability upon decompression should be caused by the higher pressures used in our experiment. On this basis, we envisage the joint use of high pressures and void space architectures as a route to materials unattainable at standard conditions yet stable upon decompression and useful for real-life applications.

We showed herein that high-pressure combined to spatial confinement could shape simple molecular blocks into 2D supramolecular networks. By using an ethanol-water mixture as pressure medium, we forced the organization of water and ethanol in distinct domains of the very restrictive pore structure of the hydrophobic zeolite ferrierite. The unique architecture here realized, made by ethanol dimer chains and water tetramers, is specific of this zeolite type, and might rationalize the high selectivity of Si-FER in the separation of alcohol-water mixtures[19] - a key issue in biofuel production.[20] Moreover, as ferrierite, in its hydrophilic Bronsted-acid form, is an exceptionally selective catalyst for biofuel syntheses[21] but only its pore entrances are actually exploited,[21d] we might speculate that pressure, by forcing the intrusion of reactants, could also be beneficial for the catalytic performance.

Finally, the realization of pressure-induced supramolecular aggregates shaped by the pores structure of zeolites is a new and general idea, and the present study a proof-of-principle of its feasibility. Our strategy, based on pressure-enhanced confinement and experiment-theory synergy, could be applied to other void architectures to create materials where organization of guest molecules or nano-objects is determined by the joint effects of high pressure and shape restraints. In this respect, the topology and chemical nature of the framework, so as the composition of the pressure medium, play a key role. Understanding the effects of these factors, and how molecular organization evolves with increasing pressure, could be the first steps towards an atomistic description of pressure-driven intrusion and organization processes, fundamental for perspective applications.

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Keywords: density functional calculations • high-pressure chemistry • self-assembly chemistry • X-ray diffraction • zeolites

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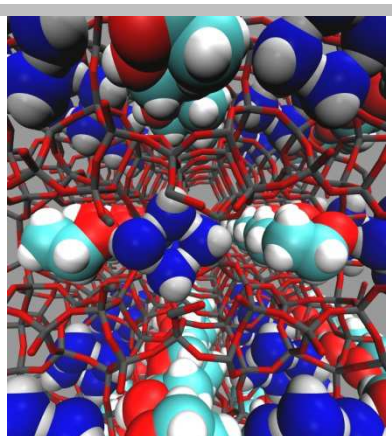
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COMMUNICATION

At high pressure, an ethanol-water solution injected in a hydrophobic nanoporous container separates into supramolecular blocks of its constituents - ethanol rows and water squares – arranged in a two-dimensional network (see image). The architecture remains stable on returning to room conditions, showing that pressure-enhanced confinement can shape mixtures of simple molecules into organized materials.



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Irreversible Conversion of a Water–Ethanol Solution into an Organized Two-Dimensional Network of Alternating Supramolecular Units in a Hydrophobic Zeolite under Pressure