

Another approach to address perovskites' thermal stability is to use inorganic perovskites such as CsPbX₃, where the cesium (Cs) cation is less volatile. There has been growing interest in perovskites for light-emitting field-effect transistors and phototransistors. By integrating organic and inorganic cations, a research

team has made a triple cation perovskite Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb(Br_{0.17}I_{0.83})₃ that has low amounts of electronic defects and better thermally stability.

Mohammad Khaja Nazeeruddin of the École Polytechnique Fédérale de Lausanne, Switzerland, Jin Jang of Kyung Hee University in South Korea, and their

colleagues used the new material to make field-effect transistors that have mobilities over 2 cm²/V-s and inverters with voltage gains over 20. The researchers say that these are the best reported performances of such perovskite devices. The work is reported in *Advanced Materials* (doi:10.1002/adma.201602940).

Researchers at Florida State University have made a new organic–inorganic metal halide perovskite with a one-dimensional (1D) structure. The material has a 1D perovskite structure where the edge-sharing octahedral lead bromide chains [PbBr₄⁻²]_n are surrounded by columnar cages formed by an organic

cation (C₄N₂H₁₄²⁺) to form core–shell wires. Millions of these wires are stacked together to form a crystalline bundle.

The 1D structure is excellent at trapping electron–hole pairs called excitons. This leads to efficient bluish white-light emissions with photoluminescence quantum efficiencies

of approximately 20% for the bulk single crystals and 12% for the microscale crystals, as reported in *Nature Communications* (doi:10.1038/ncomms14051). The material could open up a new way to make efficient light-emitting devices and phosphor materials for display applications.

High pressure and small spaces create order from disorder

Geologists have long studied the effects of high pressure on water in the porous media of rocks and minerals in the earth's crust, mainly to explore deformation properties. Now Gloria Tabacchi, a computational chemist at the University of Insubria, Italy, has enlisted the help of her earth science colleagues to study the effects of high pressure on an ethanol/water solution in the channels of a zeolite. The result is a new material that separates ethanol dimers in one channel of the zeolite and water tetramers in another channel. Perhaps most significantly, the material maintains its structure when the pressure is removed, opening up the possibility of room temperature, ambient pressure devices that could separate more complex molecules for various applications, such as solar energy conversion.

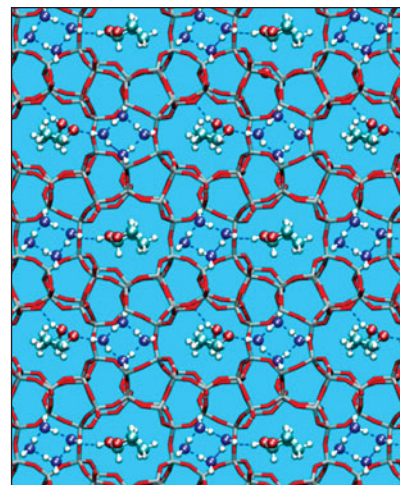
“Usually, when you create something under pressure, all the interesting properties disappear when you release the pressure,” Tabacchi says. “So this was a very nice surprise.”

In this proof-of-principle research published in a recent issue of *Angewandte Chemie* (doi:10.1002/anie.201610949), the investigators chose a simple ethanol/water solution because it was easier to

study experimentally and computationally. Also, the solution is not explosive at high pressures. They chose the hydrophobic all-silica zeolite ferrierite (Si-FER, formula Si₃₆O₇₂) because it has channels that intersect to form two-dimensional (2D) arrays, along with the right diameters to contain the ethanol and water molecules. They hypothesized that high pressure might enhance the shape-directing action of the zeolite matrix, triggering the formation of organized arrangements.

Experimentally, the geologists, led by Rossella Arletti of the Department of Earth Sciences at the University of Turin, Italy, injected a 1:3 solution of ethanol and water into the zeolite at pressures ranging from 0.20 to 1.34 GPa using a diamond anvil cell. They analyzed the resulting material using high-pressure synchrotron x-ray powder diffraction. At 0.84 GPa, the x-ray analysis showed the inclusion of four ethanol molecules and 6–8 water molecules per unit cell.

Taking the experimental data as a starting point, Tabacchi and colleagues used density functional theory and molecular dynamics simulations suitable for complex organic–inorganic systems. To determine precisely the number of water molecules per unit cell, the computational chemists built Si-FER models containing four ethanol molecules and a range of 6–14 water molecules per unit cell.



Ethanol dimers (cyan, red, and white ball-and-sticks) and water tetramers (blue and white ball-and-sticks) in Si-ferrierite (gray and red sticks). Dotted lines indicate hydrogen bonds. (Image created with VMD: www.ks.uiuc.edu.)

Density functional theory-based structural optimizations showed that the lowest energy (most stable) structure contained eight water molecules per Si-FER unit cell.

Further study of the model revealed that the ethanol molecules formed wires of hydrogen-bonded dimers, while the water molecules formed square tetramers with a closed chain of strong hydrogen bonds. Surprisingly, the zeolite/water/ethanol structure remained stable when



the simulation was performed with the cell parameters found experimentally when pressure was fully released.

“At first, we hadn’t checked the material to see if it had remained the same at ambient pressure,” Tabacchi says. But the experimentalists quickly confirmed that the ethanol dimers and water tetramers were still in place in the zeolite channels at ambient pressure. This validated the discovery. “We had taken a disordered liquid solution and converted it into a new material—a solid with a normal distribution of water and ethanol,” Tabacchi says.

The researchers theorize that perhaps the high pressure causes some slight modification of the structure that makes the material stable at ambient pressure as well. Separating ethanol from water is a key issue in biofuel production, so this zeolite might have a practical application. Tabacchi envisions trying more complex systems with a different zeolite to accommodate molecules of larger size, like the chromophores of a dye, to create a material featuring a 2D arrangement of photoactive molecules that perhaps can capture solar energy more efficiently than is now possible.

“Beautiful and fascinating” is how Gion Calzaferri, a professor in the Department of Chemistry and Biochemistry at the University of Bern, Switzerland, who was not involved in this research, describes the work. “The discovery of this host–guest composite allows us to dream about materials having fascinating physical (and perhaps also chemical) properties we have not seen so far. It may be the beginning of a new area of research exploring one-dimensional nanomaterials based on two different parallel running molecular wires.”

Tim Palucka

Finite-difference methods used to model photonic wave localization in 3D quasicrystals

Scientists at the Korea Institute of Science and Technology (KIST), led by Kayhun Hur, have made the first theoretical demonstration of the localization of photonic waves in a three-dimensional (3D) quasicrystal. This promising finding suggests that quasicrystals could one day be precisely engineered to control localization of electrons, phonons, and photons.

Quasicrystals are a unique type of crystalline material with local order but no long-range periodicity. The discovery of these materials in aluminum-manganese alloys garnered materials scientist Dan Shechtman the 2011 Nobel Prize in Chemistry. Quasicrystals exhibit unusual properties due to their mixed structural characteristics. Because translational symmetry strongly governs the transport properties of every form of wave, wave transport in quasicrystals—including localization—has been a long-standing area of research interest. In particular, icosahedral quasicrystals possess a 3D photonic bandgap, which could allow for control of light at the nanoscale.

In crystalline materials, waves with wavelengths commensurate with the crystal’s periodicity can transmit without scattering loss, leading to ballistic transmission. In contrast, because of frequent scattering, wave transport in disordered materials is usually described by random walks, resulting in diffusive transmission. Quasicrystals exhibit both diffusive transport due to their aperiodicity, along with a well-defined coherent path due to their crystalline nature. These materials therefore provide a compelling test system to investigate wave localization in three dimensions.

As reported in a recent issue of *Nature Physics* (doi:10.1038/NPHYS4002), the KIST team used finite-difference methods to model photonic wave localization in a 3D icosahedral quasicrystal. Wave localization phenomena were investigated by

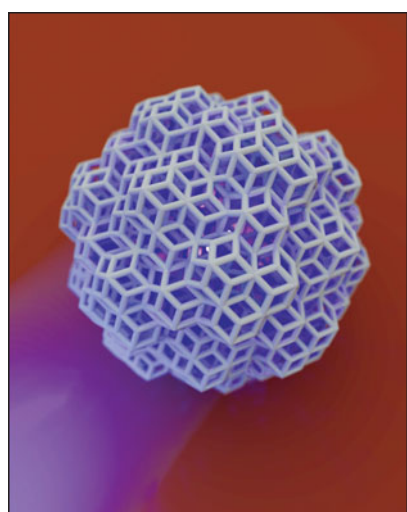
analyzing the spatial and temporal evolution of photonic waves. Using photonic band structures of quasicrystals called rhombic triacontahedrons (see Figure), the research team generated transmission spectra and compared these to a diamond structure for reference. Their findings demonstrate that wave localization occurs in quasicrystalline materials. This fundamental insight will help researchers to determine how to control or steer waves in quasicrystals.

“This proof-of-principle study breaks new ground by showing that it is possible to localize photonic waves even in a disorder-free medium solely relying on the absence of translational invariance in quasicrystals,” says Bohm-Jung Yang of Seoul National University in South Korea, who was not involved in the research.

Hur and colleagues suggest that wave localization in quasicrystals can be utilized for a variety of applications related to wave transport: replacing reflecting mirrors in lasers, incorporating quasicrystalline nanostructures into thermoelectrics as phononic insulators to improve the thermoelectric figure of merit, or as acoustic insulators. In addition, the superior wave trapping properties of quasicrystals make them excellent candidates as light-trapping layers in photovoltaics.

“Due to the universal features of wave transport in 3D quasicrystals, we believe there will be other, huge potential applications of these materials based on control of wave localization,” Hur says.

Aditi Risbud



Schematic representation of photonic wave localization in a three-dimensional icosahedral quasicrystal. Incident photonic waves are trapped in the quasicrystal due to localization. Image courtesy of Kahyun Hur, Korea Institute of Science and Technology.