

The light emission lifetime from a family of perovskite-like tin halides depends strongly on temperature, researchers reported in the journal *Nature Materials* (doi:10.1038/s41563-019-0416-2). They used the materials to make a high-resolution remote thermal imaging device.

Thermal imagers are used in medicine, defense, and security cameras and to inspect buildings and pipelines. Conventional devices detect infrared

radiation from objects. But another promising approach is to use temperature-sensitive photoluminescent materials that emit visible light. These materials can be integrated into objects as temperature probes. To measure the object's temperature, the material is hit with laser pulses, and then the temperature-dependent photoluminescent decay is measured. These emitters need to be thermally sensitive (less than 0.1°C) over a large temperature range.

After testing several tin halide perovskite compounds, ETH Zürich's Sergii Yakunin and Maksym V. Kovalenko and their colleagues shortlisted three materials with suitable thermographic properties. The materials could reproducibly measure temperature down to 0.013°C over a range of 100°C. Using low-cost hardware for fluorescence lifetime imaging, the research team was able to use one of the perovskites (C<sub>4</sub>N<sub>2</sub>H<sub>14</sub>I)<sub>4</sub>SnI<sub>6</sub> to make a sensitive, real-time thermal recording.

### Nacre-inspired composites display optical transparency, fracture toughness

Inspired by the structure of mother of pearl (nacre), researchers from ETH Zürich have demonstrated an approach to fabricating optically transparent composite materials that are tough, strong, and wear-resistant—normally an elusive combination. As they reported in *Nature Communications* (doi:10.1038/s41467-019-10829-2), the composites have some of the highest strengths among glasses and a fracture toughness up to three times greater than that of common glasses.

Optically transparent materials such as silica- and soda-lime glasses are strong enough to withstand heavy loads, but they are prone to shattering—cracks spread quickly due to their brittle nature. Chemical and thermal treatments can increase the strength of a material but not its resistance to crack propagation, a property associated with fracture toughness. Recently, research has demonstrated that engraving microstructures on a brittle glass surface can increase its fracture toughness, but the microstructures act as defects that reduce the material's strength.

Led by André R. Studart and Florian Bouville (now at Imperial College London), the ETH team took a nature-inspired approach to designing a material that is tough yet strong. The inside of mollusk shells and the outside of pearls are composed of nacre, a strong, tough, iridescent material. This combination of properties is achieved via a two-pronged

approach: a chemical composition that offers optical functionality and a complementary microscale architecture that adds toughness to an otherwise brittle material. Studart calls this approach “a pathway to combine, in a single composite material, contradicting properties that would not be achievable using conventional approaches.”

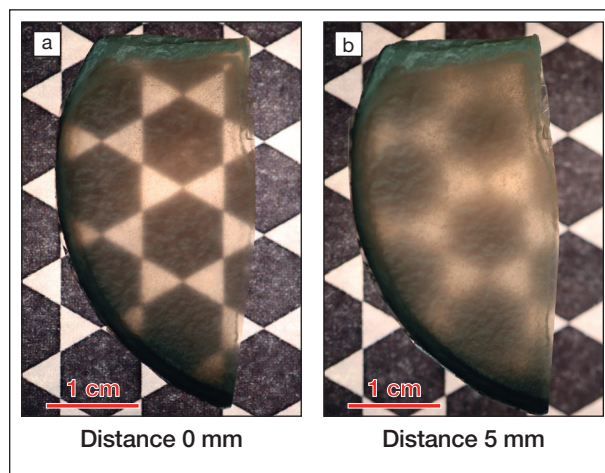
Nacre is an inorganic–organic composite with a layered brick-and-mortar structure. Calcium carbonate “bricks” are linked together by thin mineral bridges and surrounded by a “mortar” of biopolymers. Research shows that this design adds toughness to a material, promoting crack bridging, deformation, and other behaviors that slow crack propagation.

To create a similar structure in an optically transparent material, Tommaso Magrini, a graduate student working with Studart, fabricated composites from silica glass flakes and a polymeric mixture of poly(methyl methacrylate) (PMMA) and phenanthrene (PHN) with the same index of refraction as silica. The glass flakes were dispersed in water and slowly settled into horizontally aligned layers. Then the material was dried, uniaxially compacted, and sintered to create bridges at the points

where neighboring flakes were in contact. The result was a glass scaffolding of interconnected silica “bricks,” similar to the calcium carbonate structure seen in nacre. The polymeric mixture then infiltrated the scaffolding and was polymerized *in situ*.

By exposing the composites to different compressive strengths before sintering, the researchers were able to tune the density of the silica scaffolding. Their characterizations focused on composite samples with 35%, 45%, and 59% silica content by volume.

Mechanical tests showed that composite strength increased with silica content. At 59% silica content, composites displayed the strength of common glasses and transparent polymers. Their surface hardness was an order of magnitude lower than that of silica glass, but at



Nacre-based composite (59% silica content by volume) that is (a) in contact with and (b) 5 mm above a backlit pattern. Credit: Magrini et al., *Nature Communications*.



least 10 times higher than that of transparent polymeric materials. Furthermore, the team found that cracks caused less structural damage to the new composites than to harder glasses. Bending tests and high-resolution imaging revealed that the fracture resistance of the composites increased with crack growth, yielding fracture toughness 2.5–3 times greater than that of common glass.

In the visible range, the researchers measured a total diffuse transmittance of 45–55% for 1-mm-thick samples. This is significantly less than typical optical glasses, but the researchers expected that

optimizing the infiltration process could partially reduce the difference. Optical characterizations also revealed a significant hazing effect, likely due to air pockets in the material. This makes it best suited for applications close to a light source, such as protective display covers, say the researchers. They hope this research will spur efforts to quantify the structure–property relationships of the material, which could lead to enhanced mechanical and optical properties and a wider range of applications.

The ETH approach offers a simple and scalable route to bulk materials with

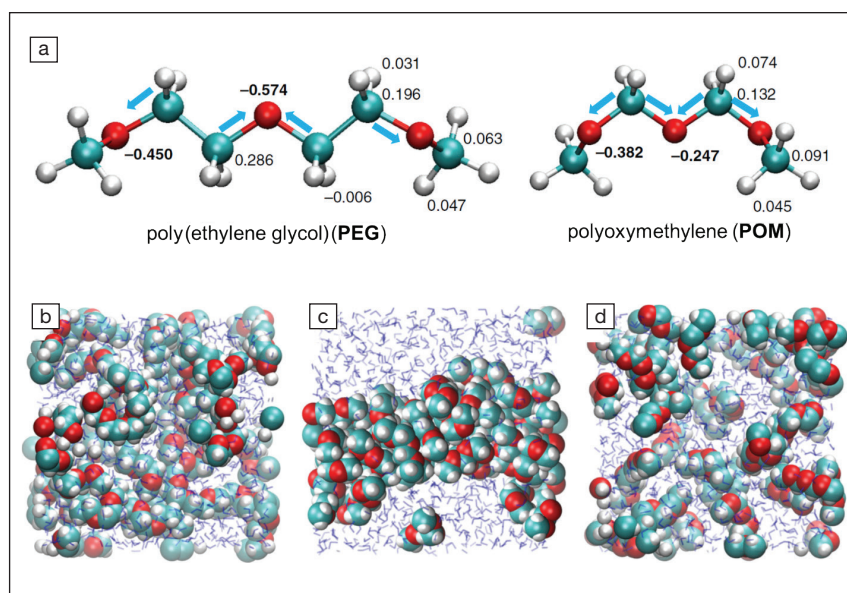
a remarkable combination of transparency, strength, and toughness, according to Flavia Libonati, an expert in the toughening mechanisms of biological structural materials at the Politecnico di Milano. “This work demonstrates the possibilities of implementing microstructural nacre-like toughening mechanisms into glass-based materials, overcoming the intrinsic limitations of such materials, for example, brittle fracture, and offering a valid alternative to silica-based glasses for numerous applications,” she says.

**Kendra Redmond**

### The puzzle of water solubilities of polyethers solved

The anomalous water solubilities of polyethers have long puzzled researchers. Typically, increasing the oxygen-to-carbon ratio of an organic compound enhances its water solubility. This principle, however, is invalid in the case of polyethers. Polyoxymethylene (POM), a polyether with one carbon atom and one oxygen atom in its repeating unit ( $[-CH_2-O-]_n$ ), is entirely insoluble in water. In contrast, poly(ethylene glycol) (PEG), a polyether having two carbon atoms and one oxygen atom in its repeating unit ( $[-CH_2-CH_2-O-]_n$ ), is infinitely water soluble. The origins of the polyethers' counterintuitive water solubilities have remained a mystery for decades.

Recently, a research team at the University of Amsterdam in The Netherlands led by Bernd Ensing and Sander Woutersen, together with Johannes Hunger and Mischa Bonn of the Max Planck Institute for Polymer Research in Germany, has shed light on this solubility puzzle for polyethers. Combining spectroscopic and computational techniques, the researchers concluded that the difference in the oxygen charge density dictated the water solubilities of polyethers. This was published in the journal *Nature Communications* (doi:10.1038/541467-019-10783-z).



(a) Atomic charges (the numbers) of poly(ethylene glycol) (PEG) (left) and polyoxymethylene (POM) (right). The blue arrows are directions of electron-withdrawing forces. (b–d) Snapshots of the atom positions of (b) PEG molecules, (c) POM molecules, and (d) POM molecules with oxygen charge equal to that of PEG oxygen. Red, blue, and white spheres represent oxygen, carbon, and hydrogen atoms, respectively. The blue V-shaped sticks are water molecules. Credit: *Nature Communications*.

Computational simulations indicated that the oxygen atoms in PEG were more negatively charged than those in POM. Due to different electronegativities, oxygen atoms pull valence electrons from neighboring carbon atoms. In POM, only one carbon atom segregates two adjacent oxygen atoms. This central carbon atom thus experiences electron-withdrawing force simultaneously exerted by the two side oxygen atoms. The opposite directions weaken the two attractive forces. Whereas

in PEG, two carbon atoms divide adjacent oxygen atoms. Each oxygen atom thus attracts electrons from its immediate neighboring carbon atom, with little competition from its oxygen neighbors. Thus, the oxygen atoms in PEG are more negatively charged than those in POM.

This discrepancy in the oxygen charge density influences the extent of water solvation, and consequently, the water solubility. Due to the more negatively charged oxygen atoms, PEG forms stronger hydrogen