constructed chiral anionic layers based on the bridged metal centres. The synthesis involves a subtle enantioselective interaction between a solution of enantiopure cations and a racemic mixture (equal amounts of the two enantiomers) of the metallic components. The reaction leads to the formation of the desired enantiopure chiral ferromagnetic layers within single crystals, with the absolute configurations of the metal centres controlled by the chirality of the enantiopure organic cations.

These chiral crystals did indeed show the hoped-for large magneto–chiral dichroism in the ferromagnetic phase, with equal and opposite signals for the two enantiomeric forms. In the paramagnetic phase a weak dichroism is observed, which increases rapidly through the paramagnetic-to-ferromagnetic transition at the Curie temperature of 7 K, increasing by a factor of 17 between 11 K and 3 K, and closely following the thermal variation of the magnetization[3].

This research has demonstrated the importance of ferromagnetism for generating large magneto–chiral effects. Owing to the bistability inherent in a magnetically ordered state, ferromagnetic chiral media could be exploited for data storage with detection based on magneto–chiral dichroism rather than magnetic circular dichroism (the Faraday effect in absorption). If they are also conductors, large values of magneto–chiral anisotropy in conduction[1] can be expected in chiral ferromagnetic materials, which could be relevant to, amongst other things, magneto–resistive sensors. The work by Train and colleagues provides a paradigm for how close interactions between chemists and physicists can lead to new rationally designed multifunctional materials, and opens the door to a whole new realm of phenomena and applications supported by magneto–chiral materials.

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BIOLOGICAL MATERIALS

Fishing for compliance

Multiscale experimental and computational approaches reveal how an ancient fish protects itself with an armour of scales consisting of four different reinforcing, graded nanocomposite layers.

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Nature is a master in the design of complex hierarchical materials in the plant and animal kingdom[1,2]. These assemblies have various functions including, perhaps most importantly, the maintenance of structural integrity when the living organism is challenged by external forces. In this struggle for survival, avoiding being eaten by predators is undoubtedly essential. It seems obvious how a tortoise[3] protects itself from becoming lunch, but not all animals can afford to carry such heavy shell armour around.

Fish began armouring themselves around 500 million years ago[4] in response to predatory threats and, to improve manoeuvrability and speed, their armour has evolved into finer and lighter dermal armour plates[5]. On page 748 of this issue, Ortiz *et al.* investigate the elaborately constructed scales and the fascinating overall approach by which a fish protects itself[6]. An inner layer of the scales, which is compliant, or more yielding to an applied force, is key in the protective mechanism. An understanding of the structure–property relationships of fish scales has broad implications for the development of impact-resistant materials, for example in bio-inspired body armour for humans.


CHRISTINE ORTIZ

Figure 1 *Polypterus senegalus.* A species of fish that belongs to the Polypteridae family that is thought to have originated during the Cretaceous period. This 'living fossil' has many of the same biological characteristics as its ancestors.

Polypterus senegalus is an ancient fish that today lives at the bottom of freshwater, muddy shallows and estuaries in Africa[7] (Fig. 1). It is described as ancient because it belongs to a family of fish, called Polypteridae, that appeared ~96 million years ago and it maintains many of the biological characteristics of its forefathers. For self-protection, this fish has armour that consists of scales. Each scale consists of four different layers of organic–inorganic nanocomposites[8] (from outer to inner surfaces): ganoine enamel, dentine, isopedine and a bone basal plate (Fig. 2). These layers vary in thickness from ~10 μm for ganoine to ~300 μm for the bone plate. Up to now, however, little has been known about the structure–property relationships of the scales and their constituent layers, and crucially, their function following a predatory biting attack.

Using nanoindentation, a method that measures the resistance of the layers to mechanical deformation with high depth resolution, Ortiz and colleagues were able to show that the indentation modulus, which is roughly a measure of stiffness, as well as the hardness, decreases from the scales' outer to the inner surfaces. These properties correlate with the structure of the layers: The mineral content (apatite) decreases and the collagen content increases between each successive layer for the first three layers, that is, in the order of ganoine, dentine and isopedine. The ganoine layer contains less than 5% organic material and consists of rod-like pseudoprismatic apatite crystals whereas the isopedine layer consists of superimposed orthogonal collagenous layers forming a plywood-like structure. The basal bone plate is composed of a series of vascularized bone lamellae with the collagen fibrils approximately oriented parallel to the scale surface[8].

Interestingly, the decrease of modulus and hardness from the outer to inner surfaces of the ganoine and the dentine layers is approximately linear. A decrease of modulus and hardness was found at the ganoine–dentine junction and also the dentine–isopedine junction. The junction between the dentine and the isopedine layers is corrugated.

Using finite element analysis, a computational method to simulate and visualize mechanical properties, Ortiz and colleagues calculated the indentation modulus and the yield stress, which can be considered as the stress when the material 'gives'. The yield stress decreases between each of the four layers (from the outer surface in) by a factor of ten. In turn, the energy dissipation during indentation increased by a factor of four, indicating that more energy is required to penetrate the deeper layers, when a predator tries to bite through the scales.

The fish's main 'trick' in its macroscopic defence is the microlayered structure, however, and not the gradients within the layers. This quad-layer microstructure provides a load-dependent stiffness and hardness, which is not the case for homogenous systems. The indenter used in this method and the tooth of a predator in a real-life situation, both 'sense' a more compliant dentine layer as they apply a load on the outer ganoine layer of the fish's scale. The gradients at the junctions between the ganoine and dentine layers and between the dentine and the isopedine layers are, however, far from redundant. These gradients provide an effective transitional region for stress redistribution between the layers, mitigating interface failure and increasing the penetration resistance. On indentation, the stiff ganoine transfers the load through the ganoine–dentine junction. The more compliant dentine layer dissipates energy via plasticity. The ideal thicknesses of the layers in combination with their materials properties enables this favourable effect and means that a circumferential cracking of the ganoine is preferred to radial cracking of the surface. The radial cracking would be disadvantageous, as a crack at the surface would further propagate leading to a more extended failure of the scale surface compared with a local puncture observed in circumferential cracking. The corrugation at the junction of the layers helps to distribute stress and raises delamination resistance of the interface.

These investigations show that fish scales possess a fascinating reinforcement mechanism that is based on a natural composite, structured through a juxtaposition of multiple reinforcing layers. Each layer has its individual deformation and failure mechanisms based on different levels of gradation and a complex crack propagation mechanism leading to a graded line of defence. Related reinforcement and/or crack-stopping properties of bi- or multilayered structures are frequently encountered in nature, for example at the enamel–dentine interface of human teeth[9] or beetle shells[10].

Now it is important that more studies are carried out on the scales of other fish and, more generally, on materials created by nature. This is only the first step to making biomimetic manmade materials systems such as body armour or impact-protection systems for vehicles. As soon as materials scientists understand the structure and the properties, we face an even greater challenge: synthesizing and manufacturing these biomimetic systems. Nature has had several million years to perfect her designs — we have just started.

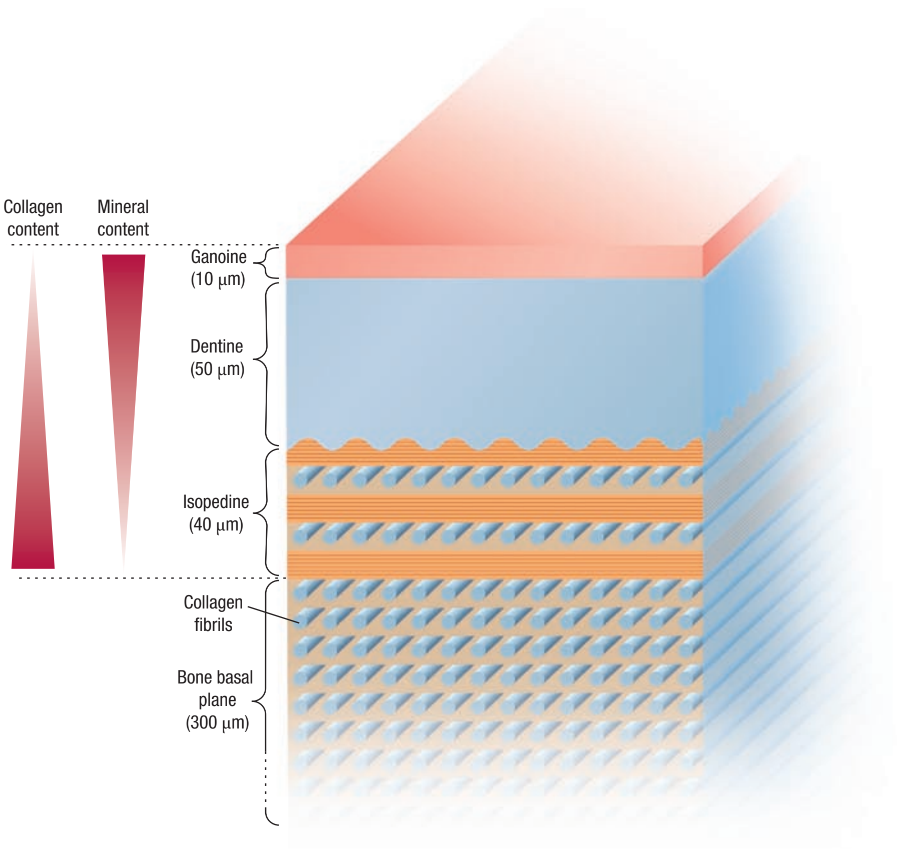

Figure 2 The four different layers that make up the fish's scales. The outer layer is composed of ganoine, the next is formed of more compliant dentine that dissipates energy plastically, the third layer is isopedine and the inner layer is formed of bone lamellae. From the outer to the inner surfaces, the mineral content decreases and the collagen content increases, for the first three layers.

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