Ressort: Special interest

Molecular ?string lights? with a quantum twist.

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Empa researchers have succeeded for the first time in binding organic porphyrin molecules with functional metal centers to a graphene nanoribbon with atomic precision. The resulting hybrid system is magnetically and electronically coupled, paving the way for a wide range of applications in molecular electronics, from chemical sensing to quantum technologies. Organic chemistry is the basis of all life on Earth.

However, metals also play a key role in many biochemical processes. When it comes to “marrying” large, heavy metal atoms with light organic compounds, nature often relies on a specific group of chemical structures: porphyrins. These molecules form an organic ring; in its center, individual metal ions such as iron, cobalt, or magnesium can be “anchored.” The porphyrin framework forms the basis for hemoglobin in human blood, photosynthetic chlorophyll in plants, and numerous enzymes.

Depending on which metal is captured by the porphyrin, the resulting compounds can display a wide range of chemical and physical properties. Chemists and materials scientists have long sought to exploit this flexibility and functionality of porphyrins, including for applications in molecular electronics.

However, for electronic components—even molecular ones—to function, they must be connected to each other. Wiring up individual molecules is no easy task. But this is precisely what researchers at Empa's nanotech@surfaces laboratory have achieved, in collaboration with synthetic chemists from the Max Planck Institute for Polymer Research.

They have succeeded in attaching porphyrins to a graphene nanoribbon in a perfectly precise and well-defined manner. The corresponding study has just been published in the journal Nature Chemistry.

A carbon “backbone”
Graphene nanoribbons are long, narrow strips of the two-dimensional carbon material graphene. Depending on their width and the shape of their edges, they exhibit a wide range of physical properties, including different conductivities, magnetism, and quantum behavior.

“Our graphene ribbon exhibits a special type of magnetism thanks to its zigzag edge,” explains Feifei

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Xiang, lead author of the study. The metal atoms in the porphyrin molecules, on the other hand, are magnetic in a more “conventional” way. The difference lies in the electrons that provide the spin responsible for magnetism. While the spin-carrying electrons in the metal center stay localized on the metal atom, the corresponding electrons in the graphene ribbon “spread out” along both edges. “Thanks to the coupling of the porphyrins to the graphene backbone, we have succeeded in combining and connecting both types of magnetism in a single system,” explains co-author Oliver Gröning, deputy head of the nanotech@surfaces laboratory.

Sense, emit, conduct

But that's not all: Porphyrins are also natural pigments, as seen in molecules like chlorophyll and hemoglobin. For materials scientists, this means that “the porphyrin centers are optically active,” says Gröning. And optics is an important way of interacting with the electronic and magnetic properties of such molecular chains. Porphyrins can emit light whose wavelength changes with the magnetic state of the entire molecular system – a kind of molecular string of lights, where information could be read out by subtle shifts in color.

This coupling opens many doors in the field of molecular electronics. The graphene ribbon serves as both an electrical and magnetic conductor – a kind of nanoscale “cable” between the porphyrin molecules. The correlated magnetism of such graphene nanoribbons is considered particularly promising for quantum technology applications, where the spin underlying magnetism acts as an information carrier. “Our graphene ribbon with the porphyrins could function as a series of interconnected qubits,” says Roman Fasel, head of the “nanotech@surfaces” laboratory.

The reverse process is also possible: The porphyrins could be excited by light, thereby influencing the conductivity and magnetism of the graphene backbone. These molecular all-rounders could even serve as chemical sensors. Porphyrin molecules can be easily functionalized – that is, chemically modified by attaching specific chemical groups. If one of these added groups binds to a target chemical substance, this interaction also affects the conductivity of the graphene ribbon.

“Our system is a toolbox that can be used to tune different properties,” says Fasel. Next, the researchers plan to explore different metal centers inside the porphyrins and investigate their effects. They also aim to broaden the graphene ribbon backbone, giving their molecular system an even more versatile electronic base. The synthesis of these “string lights” is anything but trivial. “Our partners at the Max Planck Institute were able to produce precursor molecules consisting of a porphyrin core complemented by a few carbon rings placed at exactly the right positions,” says Gröning.

These complex molecules are then “baked” at several hundred degrees Celsius under ultra-high vacuum to

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form the long chains. A gold surface serves as the “baking sheet.” This technique is the only way to achieve these nanometer-fine structures with atomic precision. With support from the Werner Siemens Foundation, the Empa team is now working to make these novel designer materials usable for future quantum technologies. (SOURCE: Empa, Federal Laboratory for Materials Testing and Research)

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