Magnetic molecules on surfaces: Advances and challenges in molecular nanoscience

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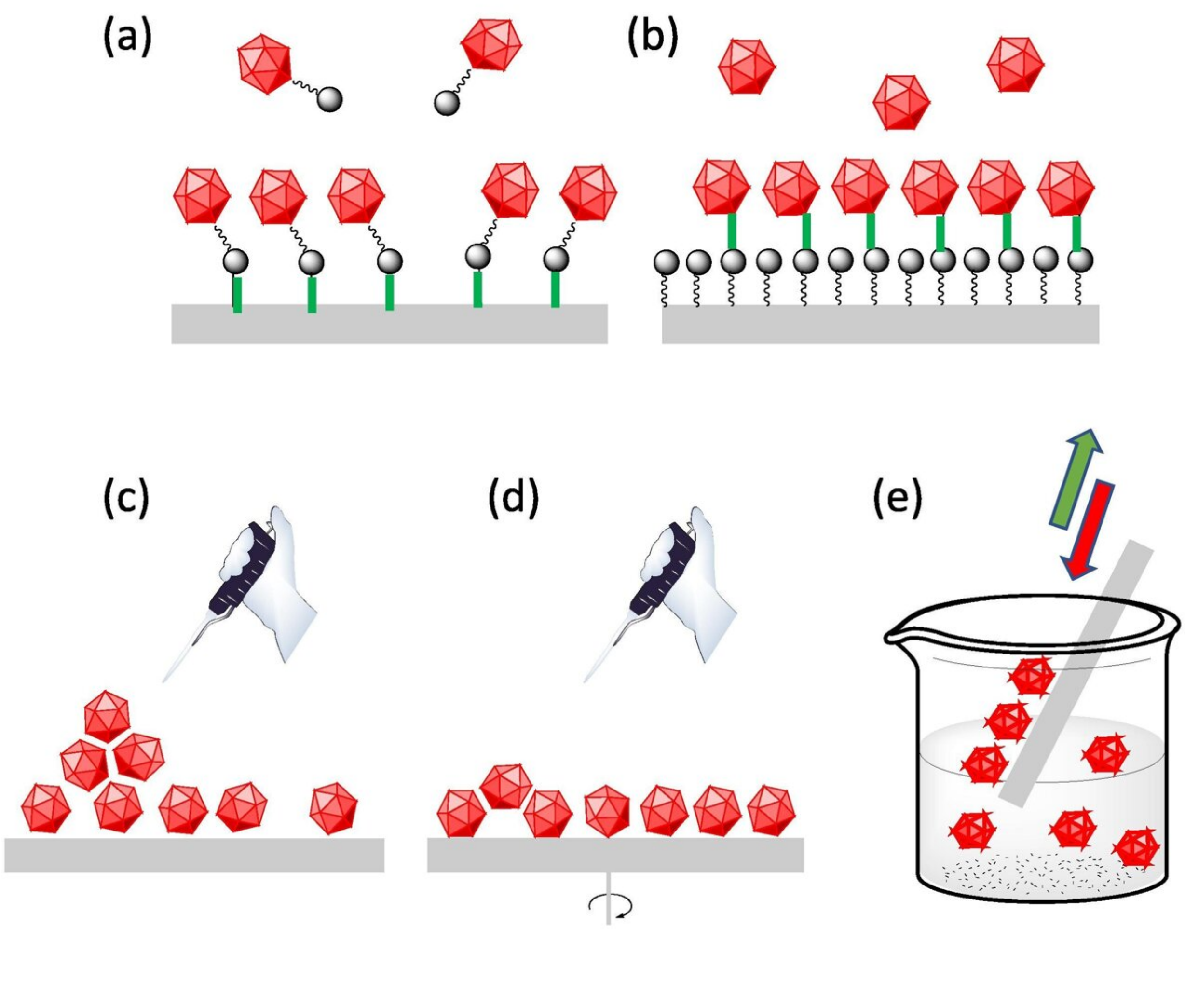

(a) and (b) show examples of chemisorption: a new covalent bond (green) is formed between the molecules (red) and the substrate via a linker (gray) attached to the molecule (a) or to the surface (b). (c), (d) and (e) show examples of physisorption by (c) drop casting, (d) spin coating and (e) dip coating. Credit: *Coordination Chemistry Reviews* (2022). DOI: 10.1016/j.ccr.2022.214858

In the field of molecular magnetism, the design of devices with technological applications at the nanoscale—quantum computing, molecular spintronics, magnetic cooling, nanomedicine, high-density information storage, etc.—requires those magnetic molecules that are placed on the surface to preserve their structure, functionality and properties.

Now, a paper published in the journal *Coordination Chemistry Reviews* analyzes the most updated knowledge on the processes of deposition and organization of magnetic molecules on surfaces (nanostructuring), a determining process for the progress of technologies that involve a miniaturization of engines and a more efficient functioning in nanometric dimensions.

The study—performed by the researchers Carolina Sañudo, Guillem Gabarró-Riera and Guillem Aromí, from the Group of Magnetism and Functional Molecules of the Faculty of Chemistry and the Institute of Nanosciences and Nanotechnology of the University of Barcelona (IN2UB)—describes the global scenario of the progress of the research in this field, and it proposes new ways to make advances in the organization in two dimensions (2D) of magnetic molecules, regarding its technological applications.

The article includes recommendations to select the best deposition method for each molecule, a review of the used surfaces in these processes, apart from guidelines for an effective characterization and future perspectives based on bidimensional materials. Moreover, the authors provide a new critical perspective on how to reach the effective application of the molecular systems in a device to get a faster technology using less energy in the near future.

Molecular nanoscience and magnetic materials

In the process to select the top deposition method on surfaces for each magnetic molecule, we have to consider each molecule and its structure, as well as the surface and structure it has. "The selection of the top method depends on the system, but it will always be possible to find a proper combination to deposit the molecular systems," says lecturer Carolina Sañudo from the Department of Inorganic and Organic Chemistry of the UB.

"The protocols vary in each case and the first step is to determine the desired characteristics of the surface," she says.

"For example, if we want to study spintronics, we will need a conducting surface. Once the surface and its nature have been determined, it is essential to determine the shape anisotropy of the molecule while looking at its crystalline structure, its properties—can it sublimate? Can it dissolve? In which solvents—and potential anchor points—does it have functional groups that allow chemisorption, and if it doesn't, what are the options for physisorption?"

"If not, what are the physisorption options? Once we have all these details, we can design a deposition protocol. For example, if our molecule has an available sulfur group, we can anchor it by chemisorption to a gold (Au) surface. If the molecule can undergo sublimation, we can do it by evaporation," she concludes.

Smaller and more efficient electronic devices

The synthesis of new molecules with better properties is an unstoppable process, "but stability does not always go hand in hand with magnetic properties. Right now, the molecule with the highest blocking temperature T—below which the molecule behaves like a magnet—is extremely unstable. In particular, it is an organometallic compound and this makes it very difficult (or impossible) to place it on the surface or use it in a technological device."

To improve the design of magnetic molecules and obtain more efficient surface deposition processes, the stability of new organometallic monomolecular magnets (SMMs) has to be improved if they are to be used effectively.

On the other hand, magnetic molecules that are not so good SMMs or that are quantum bits (qubits), or molecules that have spin-allowed electronic transitions, have features that make them very difficult to use—due to lack of or little anisotropy in their shape or multiple anchoring functional groups that make diverse depositions of the molecule on the surface possible.

"To avoid this, it is necessary to advance the organization of D2 molecules. For example, by forming two-dimensional organometallic materials (MOFs) in which the nodule is the molecule, and depositing the nanolayers that are already implicitly ordered on a surface. A 2D MOF, where each nodule is a qubit, would allow us to obtain an array of ordered qubits on a surface. This is a very important challenge and some groups like ours are working on it," the researcher says.

Reducing the energy consumption of technological devices is another goal of surface deposition technology. "The designed devices can have very low power consumption if we have a device that stores information in SMM, or we use qubits in a perfectly ordered 2D matrix, or a system with spin-enabled electronically transition—enabled molecules on a surface by molecular spintronics. In addition, they would be faster and more miniaturized than current devices."

In this field, the synthesis of inorganic compounds has generated magnet molecules that can function at temperatures around liquid nitrogen, "and this has been a major breakthrough," says the researcher. Technologies such as tunneling microscopy (STM) and atomic force microscopy (AFM) with functionalized tips are the techniques that have made it possible to identify the position of the molecules on the surface. In particular, AFM with functionalized tips can become a very useful technique to characterize surface molecules.

"The discovery that a magnesium oxide (MgO) layer of a few nanometers is needed to decouple the molecule from the surface to maintain the molecular properties once the molecule is deposited is a major breakthrough. It is also worth mentioning the coating of large surface areas by monolayers of molecules with a high percentage of order, since the arrangement of the molecule on the surface in different ways can produce different interactions and, therefore, cause not all molecules to maintain their properties."

"These two points are crucial for the future development of devices based on the use of molecules deposited on surfaces," says Carolina Sañudo.

Magnetic molecules: Future challenges

For now, obtaining SMMs at elevated temperatures, or synthesizing qubits with longer relaxation times (T1) and coherence times (T2) that facilitate use in larger devices, is a challenge for chemists. Being able to obtain large areas coated with monolayers of equal and ordered molecules will also represent a very relevant progress, and this challenge includes characterization. For this reason, the application of synchrotron light techniques—such as GIXRD, HAXPES and XMCD—will be essential.

"In order to achieve this order of the molecules on the surface, the UB Group of Magnetism and Functional Molecules is considering using 2D MOFs, i.e. coordination polymers that extend in two dimensions and are made up of extremely thin layers stacked by Van der Waals forces. Our team also wants to address other challenges, such as measuring the T1 and T2 relaxation times for a qubit deposited on a surface and confirming that they maintain (or improve) the measured values," the researcher concludes.

More information: Guillem Gabarró-Riera et al, Magnetic molecules on surfaces: SMMs and beyond, *Coordination Chemistry Reviews* (2022). DOI: 10.1016/j.ccr.2022.214858

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