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Review

Double-decker phthalocyanine complex: Scanning tunneling microscopy study of film formation and spin properties

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ABSTRACT

We review recent studies of double-decker and triple-decker phthalocyanine (Pc) molecules adsorbed on surfaces in terms of the bonding configuration, electronic structure and spin state.

The Pc molecule has been studied extensively in surface science. A Pc molecule can contain various metal atoms at the center, and the class of the molecule is called as metal phthalocyanine (MPc). If the center metal has a large radius, like as lanthanoid metals, it becomes difficult to incorporate the metal atom inside of the Pc ring. Pc ligands are placed so as to sandwich the metal atom, where the metal atom is placed out of the Pc plane. The molecule in this configuration is called as a multilayer-decker Pc molecule. After the finding that the double-decker Pc lanthanoid complex shows single-molecule magnet (SMM) behavior, it has attracted a large attention. This is partly due to a rising interest for the 'molecular spintronics', in which the freedoms of spin and charge of an electron are applied to the quantum process of information. SMMs represent a class of compounds in which a single molecule behaves as a magnet.

The reported blocking temperature, below which a single SMM molecule works as an quantum magnet, has been increasing with the development in the molecular design and synthesis techniques of multiple-decker Pc complex. However, even the bulk properties of these molecules are promising for the use of electronic materials, the films of multi-decker Pc molecules is less studied than those for the MPc molecules.

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An intriguing structural property is expected for the multi-decker Pc molecules since the Pc planes are linked by metal atoms. This gives an additional degree of freedom to the rotational angle between the two Pc ligands, and they can make a wheel-like symmetric rotation. Due to a simple and well-defined structure of a multi-decker Pc complex, the molecule can be a model molecule for molecular machine studies.

The multi-decker Pc molecules can provide interesting spin configuration. The center metal atom, including a lanthanoid metal of Tb, tends to be 3+ cation, while the Pc ligand to be 2− anion. This realizes two-spin system, in which spins from 4f electrons and π radical coexist. Though the spins of 4f orbitals of those molecules have been studied, the importance of the π radicals has been highlighted recently from the measurement of electronic conductance properties of these molecules.

In this article, recent researches on multi-decker Pc molecules are reviewed. The manuscript is organized with groups of chapters as follows: (1) Film formation, (2) Spin of $TbPc_2$ film and Kondo resonance observation, (3) Rotation of double-decker Pc complex and chemical modification for spin control, (4) Device formation using double-decker Pc complex.

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