

Syntheses of functional molecules based on porphyrin for single molecular electronics

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In these decades organic functional materials have been utilized in daily electronic products like organic light emitting diodes or liquid crystals in cellar phones or televisions. At the present stage organic materials are used as mass materials and the most characteristic properties arise from cooperative effects of the molecules. However, if each single molecule has their own specific properties and cooperate in a rational way with each other, they would emerge more sophisticated properties. With this aim, we study electronic or magnetic properties of single or small number of molecules based on porphyrin moiety, and integration of these molecular electronic parts.

Synthesis of Porphyrin-Imide Single Molecular Diode Connected to Single Wall Carbon Nanotubes (SWNT):

Our final target is making single molecular integrated circuits (molecular ICs). Wiring with more than three electrodes to the single molecules is essential to achieve it. Considering the size of the molecules, only SWNTs are the possible candidate as the electrodes. We synthesized a series of porphyrin-imide molecules (**1**) connected to SWNTs. The presence of the molecules was confirmed by AFM using gold nanoparticles as the marker. Electronic properties were measured using PCI-AFM, and their dependency on the molecular structure will be studied.

Single Molecule Magnetic Properties of a Porphyrin Based Tb^{III} Double-decker Complexes:

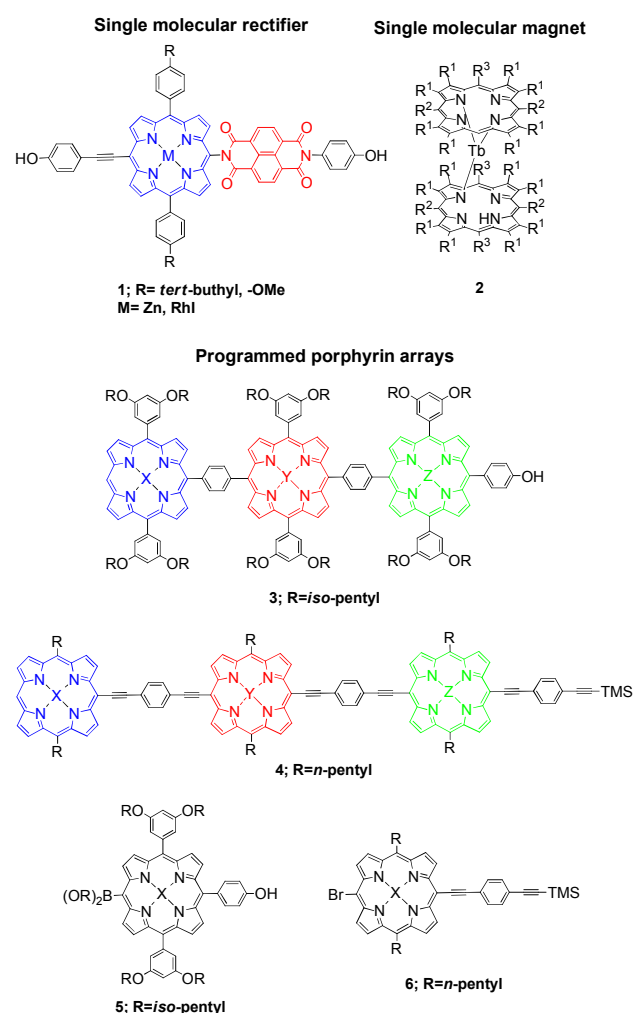
Single-molecule magnets (SMMs) have attracted wide scientific attention owing to their unique energy barrier to magnetic relaxation and their application to molecular spintronics. In the last two decades, polymetallic transition-metal complexes with strong intramolecular exchange coupling have been the typical research target because their high-spin ground state and large anisotropy may give rise to higher energy barrier than single metal ion complexes. Since Ishikawa reported single lanthanide ion based SMMs in 2003, many mono nuclear complexes showing slow magnetic relaxation have been reported. In particular, the family of phthalocyanine (Pc) based Tb^{III} double-decker compounds displays a higher blocking temperature, below which the magnetic relaxation becomes slow. Moreover, the magnetic relaxation behavior of the double-decker complexes is sensitive to their coordination mode, which can be tuned easily due to their flexible structure. This variation in their coordination modes makes it possible to control their magnetic properties by some external stimulus such as with a redox reaction or pulse current from a STM chip, resulting in unique switching properties.

A tetraphenylporphyrin based Tb^{III} double-decker complex (**2**) has been synthesized and the crystal structure of both protonated and deprotonated forms have been determined. The structure analysis demonstrated for the first time in tetrapyrrole based double-decker complexes that a proton is localized on the pyrrole ring nitrogen for charge balance. The ac magnetic

susceptibility measurements revealed that the protonated form does not show single-molecule magnet (SMM) behavior although anionic form does act as an SMM. The SMM property of the double-decker complex can be reversibly switched by only a single proton.¹

Synthesis of Porphyrin Arrays with Programmed Orders by Sequential Coupling Methods:

Once the single molecular electronic parts are prepared, they should be connected to make molecular integrated circuits (molecular ICs). One way is organic synthesis, and another way will be self-organization.² As programmable synthetic methods of the molecular parts, we developed sequential coupling reactions which are suitable for automated synthesis of complex molecules. A series of porphyrin arrays (**3**) have been synthesized using the Suzuki coupling reaction, and porphyrin arrays (**4**) by the Sonogashira coupling reaction, starting from common key compounds **5** and **6** respectively. Spectroscopic analyses of a series of **3** revealed that the order of the central metals in the arrays affected the electronic properties of the arrays greatly, which cannot be expected from the simple summation of each components.



References

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- (2) Miyake, Y.; Nagata, T.; Tanaka, H.; Yamazaki, M.; Ohta, M.; Kokawa, R.; Ogawa, T. *ACS Nano* **2012**, 6, 3876.