

SUMMARY OF Ph.D. DISSERTATION

School Fundamental Science and Technology	Student Identification Number	SURNAME, First name YAO, Masaru
Title style="text-align: center;"> Construction of π -Conjugated Molecular Self-Assemblies Having Electronic Functionality		
Abstract <p>The development, characterization, and technological exploration of new molecule-based materials, particularly as components in supermolecular system, are key challenges for modern chemistry and physics. Especially, the π-conjugated molecules have been extensively studied because of their characteristic responses to electric and magnetic fields, light, and so on. Because these properties are greatly perturbed by the molecular arrangement, it is indispensable to apply the nature of the reversible intermolecular forces for the construction of the molecular assemblies exhibiting the electronic functionality. In the present thesis, the porphyrin and quinoline derivatives bearing self-assembling moiety are systematically synthesized and the electronic functionalities of their molecular assembling systems are evaluated.</p> <p>In Chapter 2, the syntheses of five <i>meso</i>-5,15-disubstituted porphyrins carrying hydrophilic and hydrophobic groups asymmetrically and their formation of thin films at the air-water interface are described. These porphyrin derivatives form stable monolayers, and exhibit remarkably shifted patterns in the UV-vis spectra. The observed phenomenon is unique to the disubstituted porphyrins and is explained by the strong π-π interaction between the macrocycles. This study reveals the correlation between the shift of the absorption maxima and the dipole moment of the hydrophilic group at the <i>meso</i> position. In chapter 3, the magnetic properties of <i>meso</i>-5,15-diphenylmetalloporphyrins and stable nitroxyl carrying derivatives at the 10 position are described. The characteristic assembling behavior and the effects of the peripheral radical substituent on the electronic and magnetic properties of porphyrin are discussed in connection with their crystal structures.</p> <p>Taking advantage of the fundamental information about the intermolecular π-π interaction, the author focus on the magneto-structural correlation of the aromatic open-shell molecule in the solid state. The aromatic <i>N</i>-oxyl radicals have been rarely used for the study of molecule-based magnetism, since they are unstable due to a disproportionation reaction. In contrast, 2,2-diphenyl-1,2-dihydroquinoline-<i>N</i>-oxyl (QN) derivatives are fairly stable due to the delocalization of unpaired electron over the π-conjugation system and the presence of two bulky phenyl rings at the 2-position. The effect of the chemical modification of QN derivatives on the physicochemical properties are discussed in Chapter 4-6. While QN itself behaves as an isolated doublet spin center, several chemically modified derivatives exhibit strong intermolecular magnetic interactions. The direct close contacts between N-O sites which often cause a strong antiferromagnetic interaction are suppressed for all QN derivatives. Instead, polarized spin distributions over the adjacent aromatic system cause the strong magnetic interaction. The magneto-structural correlation affords some supramolecular synthons suitable for propagating the magnetic interaction in the crystal. Their electronic structures are elucidated by the MO calculation based on the density functional theory. Magnetically coupled π-stacked structures are formed by the introduction of <i>o</i>-dimethoxyl benzo or benzothiadiazole moieties. Two novel hetero biradicals based on the QN skeleton were also synthesized in order to examine the intramolecular magnetic coupling. Both of them exhibit a strong intramolecular ferromagnetic coupling, which indicates the QN skeleton can be applied to a robust spin coupler for stabilizing high-spin ground state.</p> <p>In summary, by synthesizing a series of novel compounds based on the disubstituted porphyrin and quinoline derivatives, several assembling motifs which exhibit strong electronic interactions are found. Magneto-structural correlation found in the present research will serve the design of a new molecule-based material with interesting electronic functionalities.</p>		