



**Organic Materials Chemistry**

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<http://www.sci.osaka-cu.ac.jp/chem/phyorg/POCweb/pg9.html>

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## 1. Current Research and Principal Research Interests

Our interest is centered on the fundamental understanding of electronic properties of organic and related compounds especially with open shelled electronic structures. Design, synthesis, and characterization of new p-conjugated materials toward the development of high-spin chemistry, molecular magnetism, organic and organic-based conductors, and electroluminescent devices have currently been investigated.

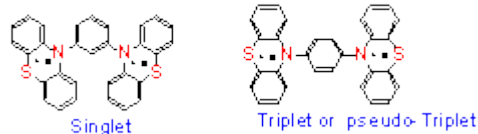
### 1) High-Spin Molecules

The study of high-spin molecules is very informative on how the electronic spins interact in the molecule. In addition, high-spin molecules are useful components as spin building blocks to prepare the magnetic materials.

#### 1-1) Heteroatomic Spin Systems

These novel heteroatomic di(radical cation)s have unique ground states.

Examples of unique heteroatomic diradical(ion)s

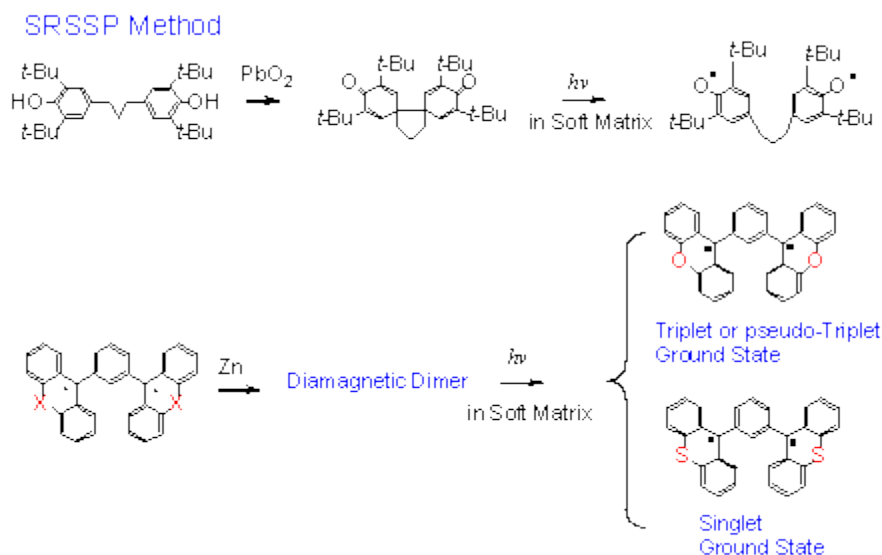


The dication 1 has singlet ground state, whereas 2 has triplet or pseudo-triplet ground state. The unique behavior can be understood as electron-delocalization effect on the lone pair electrons of sulfur atom which sits on the para-position of the spin center (nitrogen position) in the classical VB expression. The delocalization of the lone pair electrons alters the electronic nature very much and therefore the non-alternant hydrocarbon type prediction is sometimes difficult.

#### 1-2) SRSSP method

Moderately stable radicals sometimes dimerizes in solution especially at low temperature and therefore even the detection of radical species frequently fails. This is particularly true for the species with multi-radical sites. We have developed a new method called SRSSP (Sequential

Redox Solid State Photolysis) to detect such species. The method consists of the following two steps: 1) reduction and oxidation of the monomeric dication or dianion to give diamagnetic dimer or polymer type weakly bonded compounds in a solvent which can be transformed into a matrix at low temperature, 2) cleavage of the weak bonds giving the desired diradical by photolysis in the soft matrix which sometimes easily available by just cooling close to the used matrix melting point.



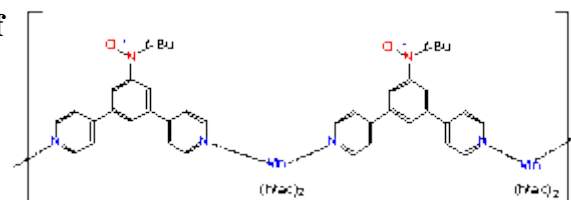
## 2) Molecular Magnetic Materials

Molecular magnetic materials (MMM) have many advantages when compared to the classical metal magnets; not only color or soft nature but also sensible nature toward outside stimulation (light, field, pressure etc). Liquid crystalline magnets, very thin film magnets, or molecular wire type magnets with quick photo-response may not be dream. To realize MMM, fundamental studies based on currently developing method and technologies; transition metal catalyzed organic synthesis, crystal engineering, supramolecular architecture etc are essential.

### 2-1) Magnetic Interaction and Molecular Size of

#### Organic Compounds;

The degree of metal-metal magnetic interaction between the metal-ligand-metal type organic-inorganic hybrid complexes is strongly dependent on the metal-metal distance. Therefore the size of over 10 diamagnetic element usually doesn't show any metal-metal magnetic interaction. Introduction of spins in the diamagnetic organic ligand may improve the poor magnetic interaction. Thus, one-dimensional chain complexes **3** were designed and prepared. We could observe the ferromagnetic interaction between Mn(II) and nitronyl nitroxide (below 10 K,  $J=+0.3$  K). The ligand without

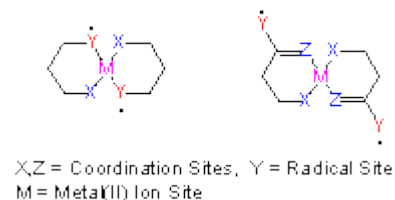


nitronyl nitroxide showed no magnetic interaction under the same conditions.

## 2-2) Spin-Ligands Synthesis;

Shortening the distance between the coordination site and the organic spin converts the above spin-introduced large bidentate ligand into spin-chelating reagents. Spin-chelating reagents can be defined as chelating reagents with organic spins. This project is now undergoing.

### Spin Chelate Concept



## 2-3) Stable Radical Introduced Radical Cations

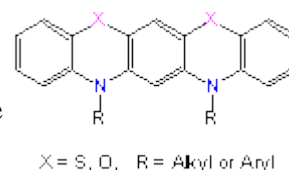
Radical substituted radical ions are expected to be superior magnetic components. Some species of this class have been synthesized. However, some species had very weak magnetic interactions between the radical ion site and the organic spin. Or some were very unstable under aerated conditions. As a result, no stable radical-substituted radical ion with strong magnetic interaction has been reported. We have recently synthesized a radical-substituted radical cation with strong ferromagnetic interaction of  $J^a +300$  K. The species was air-stable at ambient or higher temperature.

## 3) Design and Synthesis of Electronic Materials.

Electronic materials are another class of target materials. Similar to the previous magnetic materials, the design and synthesis of electronically unique p-conjugated molecules are the most important step. Organic conductors involving radical ion salts, oligomers and polymers, electroluminescent materials are currently investigated.

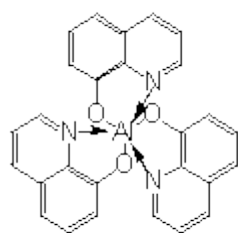
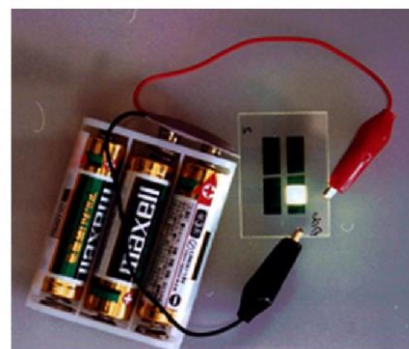
### 3-1) Charge Transfer Salts and CT-Complexes

Phenothiazine and phenoxazines are well known superior donors because of their 8 p electronic systems. The doubly condensed compounds must be much more superior donors. Hitherto, benzothiazinophenothiazine and its radicalcation has been reported. However, the isolation of the radicalcation salts has not been reported probably because of their instability. N,N-Dimethylbenzoxazinophenoxazine should have a lower oxidation potential than the corresponding sulfur analogue because of the analogy of phenothiazine and phenoxazine analogues. We have synthesized the oxygen analogues by multi-step reactions. The oxygen derivatives were shown to have superior donating properties than the sulfur analogues (0.2 V vs SCE for the sulfur N-Me derivative, +0.50 V vs SCE for the oxygen N-Me derivative). The charge transfer complexes and their radical ion salts were prepared and their solid state properties were characterized. Their conductivities were in semiconductor region ( $10^{-3}$  Å  $10^{-6}$  Scm<sup>-1</sup>).

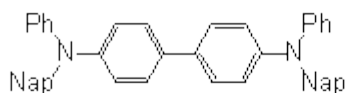


### 3-2) Electroluminescent Materials

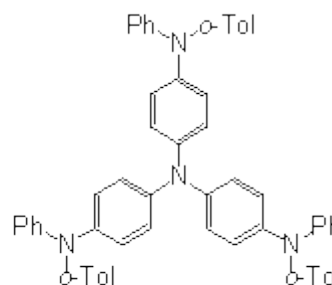
Although the above mentioned benzothiazinophenothiazine did not show good electron-donating ability, the N,N-phenyl derivative (NPD) showed a superior electroluminescent property. Two devices, ITO/DBP/NPD/Alq/LiF/Al and ITO/MTDATA/NPD/Alq/LiF/Al, were prepared and compared. NPD and Alq are typical hole transporting layer and light emitting layer, respectively. DBP was used as a hole injection layer. This type multi-layered structure was recently introduced to improve the light emitting efficiency. MTDATA is such a material to enhance the efficiency and has been used frequently. The light emitting efficiencies at 100 cd were 3.3 lm/W for DBP and 2.7 lm/W for MTDATA. Thus DBP was proved to be a better hole injection material than a typical hole injection material MTDATA.



Alq



NPD



MTDATA

### 3-3) Single Component Conducting Materials

Usually conductivity of organic compounds increases by hole injection with doping technique. However, one can imagine single component conductive molecules without doping. Such molecules should have small E1-sum. (the difference of the first oxidation and reduction potentials) as well as small HOMO-LUMO gaps in the molecular level. Molecular design and synthesis of such amphoteric molecules are within our field and we are currently doing this approach. The molecules with small E1 sum. will be also interesting from the view point of conducting magnetic materials.

### 3-4) Forthcoming Projects

Recently, two new developments have been achieved in the field of conducting materials. One is a FET (Field Effect Transistor) technological development. The FET technique is applicable to the wide range of molecules. Changing the applied voltage of FET can freely alter the doping level of molecules. As a result, some usual aromatic hydrocarbons have been converted superconductor states. We are currently going to apply the FET approach by cooperation with physicists in this university for deeper understanding molecular nature.

Another is an idea of a molecular computer. We understand this term as “a single molecule with controllable multi-functionality”. Characterization of a molecular (not bulk but a single molecule) computer certainly needs nanotechnology. The molecular computer must satisfy some fundamental requirements to be characterized by nanotechnology in addition to its own electronic nature. There are many unknown factors. However, this field can be considered as a place where material science meets nanotechnology. The development of this field is strongly dependent on the cooperation between physicists and chemists and we as chemists like to do so.

## 2. Selected Publications

1. Hiroki Mori, Osamai Nagao, Masatoshi Kozaki, Daisuke Shiomi, Kazunobu Sato, Takeji Takui, Keiji Okada, “Magnetic Behavior of Copper(II) Complexes of a Nitronyl Nitroxide-Substituted Pyrimidine”, *Polyhedron*, **20**, 1663-1668 (2001).
2. Toshihiro Okamoto, Masatoshi Kozaki, Yoshiro Yamashita, Keiji Okada, “Benzoxazinophenoxazines: Neutral and Charged Species”, *Tetrahedron Lett.*, **42**, 7591-7594 (2001).
3. Hiroki Mori, Masatoshi Kozaki, Kazunobu Sato, Takeji Takui, Keiji Okada, “A New Photochemical Approach to Benzylic Polyradicals through C-N Bond Cleavage of a Pyridinyl Radical”, *Tetrahedron Lett.*, **39**, 6315-6316 (1998).
4. Riho Suzuki, Masaji Oda, Atsushi Kajiwara, Mikiharu Kamachi, Masatoshi Kozaki, Yoshiki Morimoto, Keiji Okada, “Preparation and Characterization of Novel Organoborane Dianions”, *Tetrahedron Lett.*, **39**, 6483-6486 (1998).
5. Koji Nakatuji, Masaji Oda, Masatoshi Kozaki, Yoshiki Morimoto, Keiji Okada, “4,4'-(Trimethylene)bis(2,6-*t*-butylphenoxy) Diradical: An Application of the Sequential Redox-Solid State Photolysis (SRSSP) Method”, *Chem Lett.*, **1998**, 845-846.
6. Keiji Okada, Takaaki Imakura, Masaji Oda, Atsushi Kajiwara, Mikiharu Kamachi, Masakazu Yamaguchi, “Remarkable Heteroatom Dependence of the Spin Multiplicity in the Ground State of 9,9'-(*m*-Phenylene)dixanthyl and -dithioxanthyl Diradicals”, *J. Am. Chem. Soc.*, **119**, 5740-5741 (1997).
7. Keiji Okada, Kouzou Matsumoto, Masaji Oda, Kimio Akiyama, Yusaku Ikegami, “1,1'-(*p*- or *m*-Phenylene)bis(2,4,6-triphenylpyridinyl) Diradicals: Ground State in a Heteroatom-containing System in Relation to the Topology Rule”, *Tetrahedron Lett.*, **38**, 6007-6010 (1997).

8. Keiji Okada, Takaaki Imakura, Masaji Oda, Hisao Murai, Martin Baumgarten, "10,10"-(*m*- and *p*-Phenylene)diphenothiazine Dication: Violation of Topology Rule in Heterocyclic High-Spin Systems", *J. Am. Chem. Soc.*, **118**, 3047-3048 (1996).
9. Keiji Okada, Kazushige Okamoto, Masaji Oda, "A New and Practical Method of Decarboxylation: Photosensitized Decarboxylation of *N*-Acyloxyphthalimides via Electron Transfer Mechanism", *J. Am. Chem. Soc.*, **110**, 8736-8738 (1988).
10. Keiji Okada, Hidekazu Sakai, Masaji Oda, "Stereocontrol by Energy Transfer: Photoisomerization of  $\alpha$ -Arylalkyl Spiro-[cyclopropane-1,9'-fluorene]-2-carboxylate", *J. Am. Chem. Soc.*, **109**, 5534-5535 (1987).