

# International Research Center for Elements Science - Organic Main Group Chemistry -

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Assist Prof  
TSUJI, Hayato  
(D Eng)



PD  
SASE, Shohei  
(D Sc)

## Students

SON, Eun-Choel (D3)  
FUKAZAWA, Aiko (D2)  
INOUE, Tomoyuki (M2)

TAKASHIMA, Yohei (M2)  
KOMATSU, Shigeo (M1)

## Scope of Research

Our research is concerned with some new aspects in the elemento-organic chemistry, including (1) elucidation of the  $\sigma$ -conjugation in the polysilanes using the configuration-constrained oligosilane model systems, (2) development of intramolecular electron transfer systems through  $\sigma$ -conjugated oligosilane chains, (3) construction and application of new polycyclic systems including main group elements, (4) development of new efficient reactions using main group element reagents and transition metal complex catalysts, and (5) design and synthesis of novel  $\pi$ -conjugated systems containing main group elements.

## Research Activities (Year 2005)

### Presentations

Conformation Control of Oligosilanes Based on Bicyclic Di- and Trisilane Units, Tsuji H, Fukazawa A, Tamao K, The 38th Silicon Symposium, 2 - 5 June, Boulder, USA.

All-anti Oligosilanes: Conformation Control of Oligosilanes Utilizing the Bicyclic Trisilane Unit, Fukazawa A, Tsuji H, Yamaguchi S, Tamao K, The 14th International Symposium on Organosilicon Chemistry, 31 July - 5 August, Würzburg, Germany.

Synthesis, Structure, and Photophysical Properties of Disilatriptycene Oligomers, Sase S, Tsuji H, Kawachi A, Wakamiya A, Yamaguchi S, Tamao K, The 14th International Symposium on Organosilicon Chemistry, 31 July - 5 August, Würzburg, Germany.

### Grants

Tsuji H, Synthesis and Photophysical Properties of Porphyrin-Oligosilane Hybrid Molecules, Grand-in-Aid on

Priority Areas, April 2004 - March 2006.

Tsuji H, Establishment of Conformation Control Method of Polysilanes Based on Bicyclic Trisilane Unit, Grand-in-Aid for Young Scientists (B), April 2005 - March 2007.

### Awards

Fukazawa A, The Best Oral Presentation Award, The 85th Annual Meeting of the Chemical Society of Japan, 27 March.

Fukazawa A, Award for the First Place Poster Contribution, The 14th International Symposium on Organosilicon Chemistry, 5 August.

Fukazawa A, Student Poster Award, PACIFICHEM 2005, 18 December.

## Zinc Porphyrin–fullerene Dyad Linked by $\sigma$ -Conjugated Oligosilane Chains

Oligosilanes are regarded as a pseudo one-dimensional molecular wire and attract much attention due to their unique photophysical and electronic properties, as ascribed to  $\sigma$ -conjugation. To evaluate the electron transfer ability of the  $\sigma$ -conjugated Si–Si chain, we have developed various zinc porphyrin (ZnP)–fullerene(C<sub>60</sub>) dyads connected by oligosilane chains, shown in Chart 1. Their photoinduced processes have been studied using the time-resolved fluorescence and absorption measurements. Photoexcitation of the dyads caused energy- and/or electron-transfer from the excited-singlet state of the ZnP to C<sub>60</sub> moieties. The charge-separation takes place as the final step in the excited state process to yield the radical-ion pair with a radical cation on the ZnP and a radical anion on the C<sub>60</sub>, similar to other porphyrin–fullerene dyads. The result shows that the oligosilane chains play an important role as a good molecular wire.

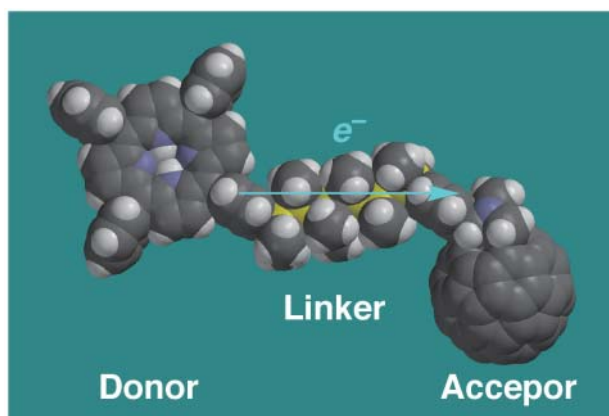


Chart 1.

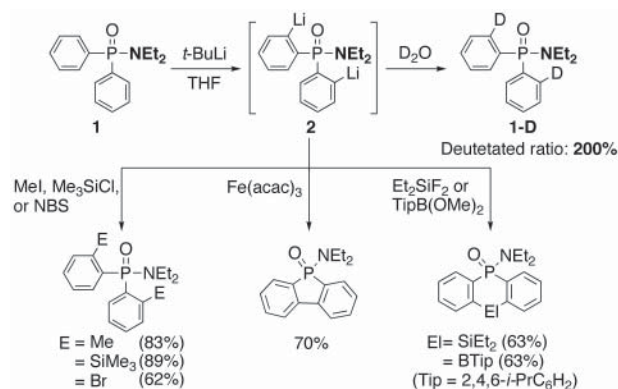
## Double ortho-lithiation of Aromatic Ring

Direct metalation on the aromatic ring is a versatile method for the preparation of functionalized aromatic compounds from the viewpoint of synthetic efficiency. Most of the preceding reports are on single-metalation, by which one aromatic ring is metalated with the assistance of the directing group. In contrast, there are a few examples regarding double ortho-metalation, where two aromatic rings are metalated simultaneously by the assistance of two directing groups. We have recently developed the methods for double ortho-lithiation of a diphenylphosphorylamide and benzophenone.

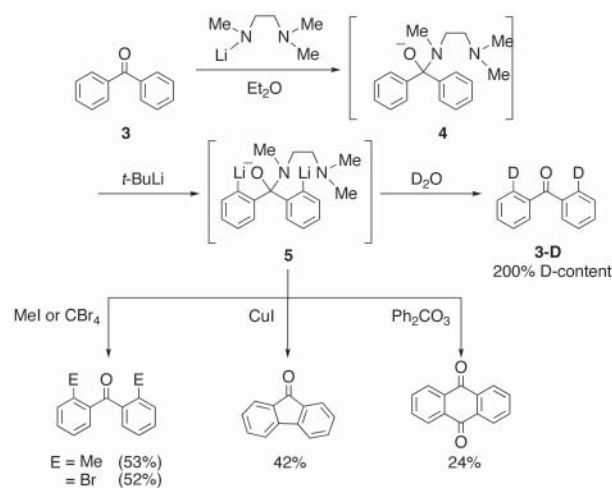
Quantitative double ortho-lithiation of phosphorylamides **1** was accomplished through treatment of **1** with

*tert*-butyllithium (Scheme 1). In this reaction, the amino moiety and the oxygen of the phosphoryl group are considered to act properly as directing groups, allowing the efficient double ortho-lithiation.

For double ortho-lithiation of benzophenone **3**, it is essential to introduce a trimethylethylenediamino moiety as an auxiliary directing group. Subsequent treatment of the resulting species **4** with *tert*-butyllithium afforded the double ortho-lithiated species **5** (Scheme 2). The double ortho-lithiated species **2** and **5** underwent the reaction with electrophiles, the intramolecular oxidative coupling to afford the five-membered ring compounds, and the intramolecular cyclization with the difunctional electrophiles to give the six-membered ring compounds.



Scheme 1.



Scheme 2.