

# International Research Center for Elements Science – Organometallic Chemistry –

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Prof  
OZAWA, Fumiyuki  
(D Eng)



Assist Prof  
WAKIOKA, Masayuki  
(D Eng)

## Students

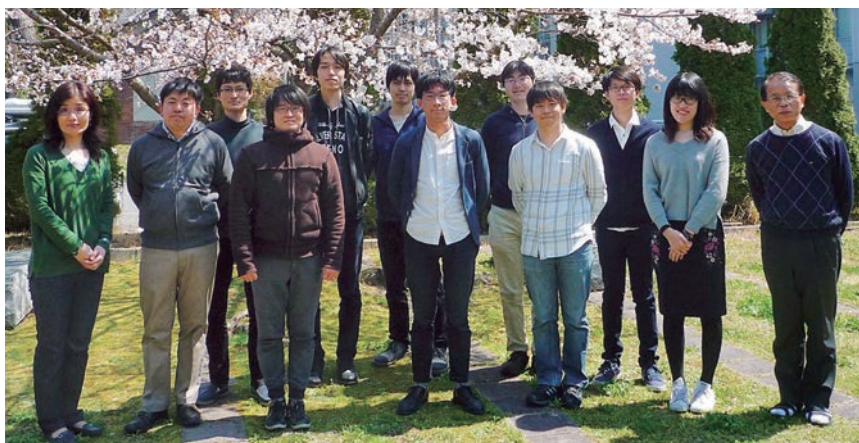
YAMASAKI, Akito (M2)    MAEDA, Junya (M1)  
TORII, Naohiro (M2)    HAMADA, Yusuke (UG)  
ISHIZUKA, Risa (M1)    MAKINO, Saiki (UG)

## Scope of Research

This laboratory aims to establish new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as spectroscopy and kinetic techniques, as well as theoretical methods. The research subjects include: 1) development of novel organotransition metal systems for catalysis based on precise ligand design, and 2) preparation of  $\pi$ -conjugated polymers using direct arylation.

### KEYWORDS

Transition Metal Complex  
Homogeneous Catalyst  
Reaction Mechanism  
Low-coordinate Phosphorus Ligand  
 $\pi$ -Conjugated Polymer

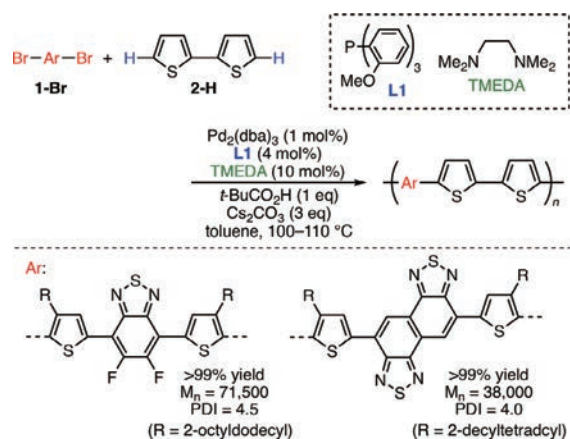


## Selected Publications

Wakioka, M.; Yamashita, N.; Mori, H.; Nishihara, Y.; Ozawa, F., Synthesis of a 1,2-Dithienylethene-Containing Donor-Acceptor Polymer via Palladium-Catalyzed Direct Arylation Polymerization (DArP), *Molecules*, **23**, 981 (2018).  
Wakioka, M.; Ozawa, F., Highly Efficient Catalysts for Direct Arylation Polymerization (DArP), *Asian J. Org. Chem.*, **7**, 1206-1216 (2018).  
Taguchi, H.; Tanigawa, I.; Takeuchi, K.; Ozawa, F., On the Geometrical Stability of Square Planar Platinum(0) Complexes That Bear a PNP-Pincer-Type Phosphaalkene Ligand (Eind2-BPEP), *Chem. Eur. J.*, **24**, 17055-17061 (2018).

## Synthesis of Benzothiadiazole-Containing Donor-Acceptor Polymers via Palladium-Catalyzed Direct Arylation Polymerization (DARp)

We found that the combined use of  $P(2\text{-MeOC}_6\text{H}_4)_3$  (**L1**) and TMEDA as ligands effectively prevented defect formation in palladium-catalyzed direct arylation polymerization (DARp) to give donor-acceptor polymers (DA polymers) with benzothiadiazole units. The reactions of benzothiadiazole derivatives (**1-Br**) and 2,2'-bithiophene (**2-H**) formed a notable amount of insoluble materials via branching and cross-linking when only **L1** was used as the ligand. In contrast, in the presence of **L1** and TMEDA, the formation of insoluble materials was completely suppressed, and the polymers with well-controlled structures and high molecular weight were obtained. The resulting polymers exhibited device performance of polymer solar cells comparable to Migita–Stille cross-coupling polymerization products.

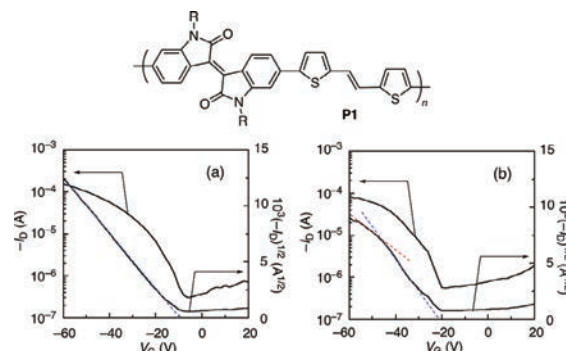


**Figure 1.** DARp synthesis of benzothiadiazole-containing DA Polymers.

## Synthesis of a 1,2-Dithienylethene-Containing Donor-Acceptor Polymer via Palladium-Catalyzed Direct Arylation Polymerization (DARp)

We found that the mixed-ligand catalyst using  $P(2\text{-MeOC}_6\text{H}_4)_3$  (**L1**) and TMEDA is effective in synthesizing DA polymers containing 1,2-dithienylethene (DTE) units via DARp. The reaction of dibromoisindigo and 1,2-dithienylethene in the presence of the mixed-ligand catalyst affords polymer **P1** with high molecular weight ( $M_n = 15,700$ ). The resulting polymer has a well-controlled structure and exhibits good charge transfer characteristics in an organic field-effect transistor (OFET), compared to the polymer produced by Migita–Stille cross-coupling polymerization. The DARp product displays an ideal linear relationship in the current–voltage curve, whereas the

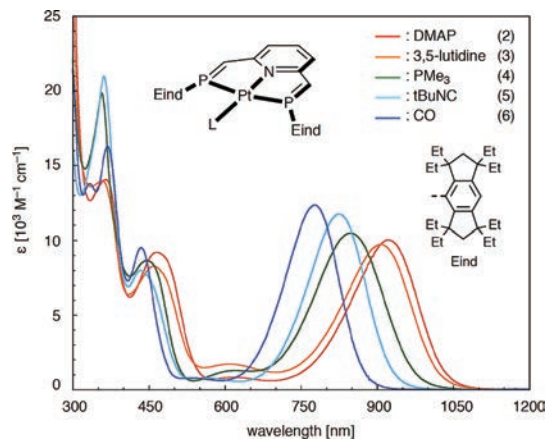
Migita–Kosugi–Stille product shows a  $V_G$ -dependent change in the charge mobility.



**Figure 2.** Charge transfer characteristics of the OFETs using **P1** prepared by DARp (a) and Migita–Stille coupling polymerization (b) ( $V_D = -60$  V).

## Square Planar Pt(0) Phosphaalkene Complexes

The four-coordinate Pt(0) complex  $[Pt(PPh_3)(Eind_2\text{-BPEP})]$  (**1**) bearing a pyridine-based PNP-pincer type phosphaalkene ligand ( $Eind_2\text{-BPEP}$ ) adopts a highly planar structure around the Pt; this coordination geometry is very uncommon for formal  $d^{10}$  metals. In this study, a series of L with different electronic properties [DMAP (**2**), 3,5-lutidine (**3**),  $PMe_3$  (**4**),  $t\text{BuNC}$  (**5**), CO (**6**)] were introduced in place of  $PPh_3$ , and their effects on the coordination geometry and spectroscopic properties were examined. X-ray diffraction analysis revealed that all complexes adopted a square-planar configuration. In contrast, DFT calculations indicated that the geometrical stability towards distortion around Pt varied with the ligand. The complexes with pyridine-based ligands had rigid planar structures, whereas those with  $\pi$ -accepting ligands, such as CO, were relatively flexible towards distortion. The electronic effects of the ligands were reflected in the spectroscopic properties of the complexes, which showed a large color change in the near-infrared region.



**Figure 3.** UV-vis-NIR spectra of  $[Pt(L)(Eind_2\text{-BPEP})]$  complexes in THF at room temperature.