

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 π -conjugated polymers using direct arylation.

KEYWORDS

Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
 π -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.

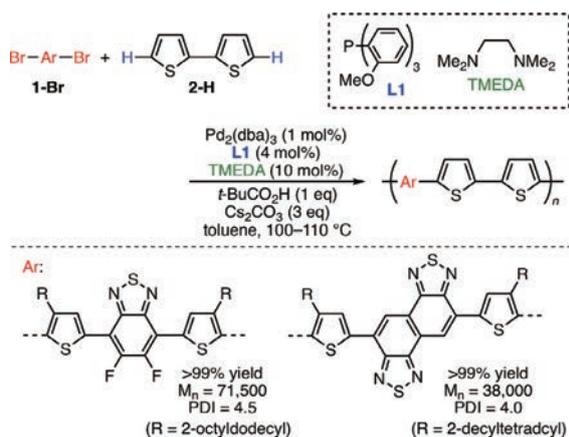


Figure 1. DARp synthesis of benzothiadiazole-containing DA Polymers.

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.

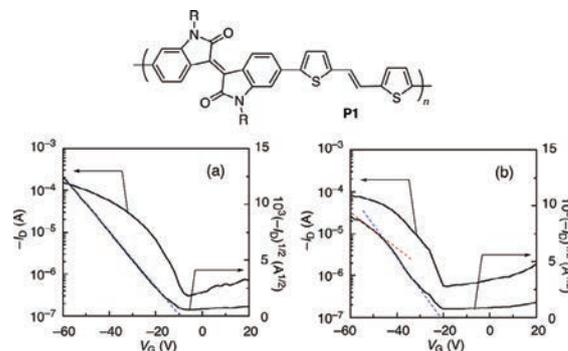


Figure 2. Charge transfer characteristics of the OFETs using **P1** prepared by DARp (a) and Migita–Stille coupling polymerization (b) ($V_D = -60$ V).

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 π -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.

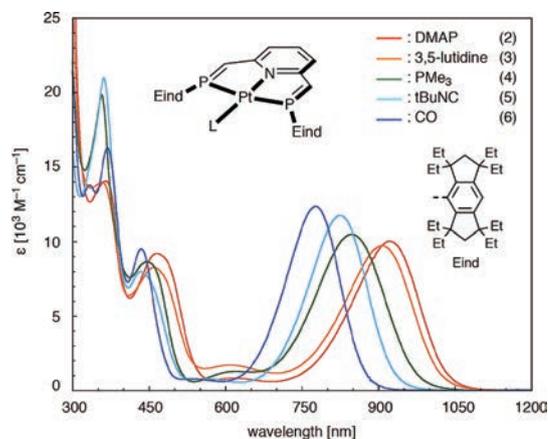


Figure 3. UV-vis-NIR spectra of $[Pt(L)(Eind_2\text{-BPEP})]$ complexes in THF at room temperature.