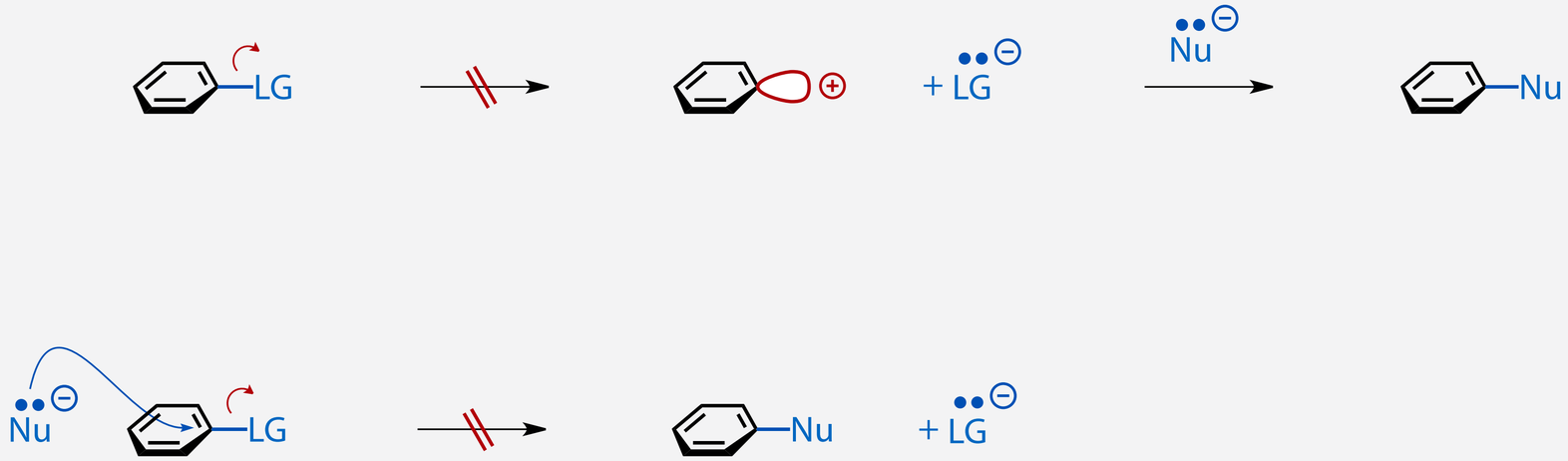
8 Organic Semiconductor Materials Preparation

Table of Contents

8.1 Synthesis of π-Conjugated Molecules

Carbon Bond Formation

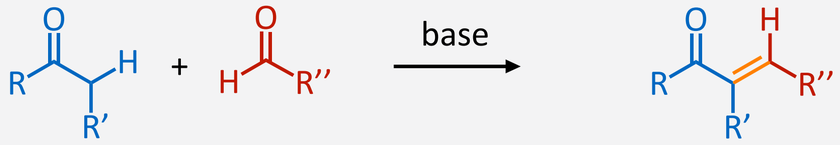
Challenges in Carbon-Carbon Bond Formation



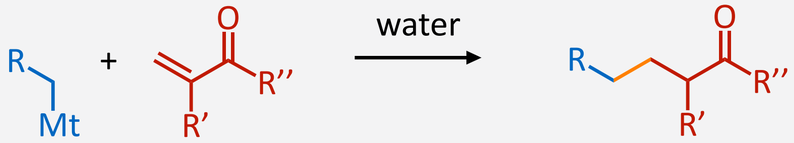
- no simple S_N1 or S_N2 substitution reactions for carbon couplings on aromatic systems

Classical Carbon Bond Forming Reactions

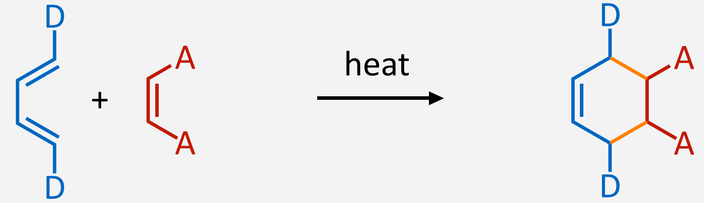
- Aldol condensations and related carbonyl reactions



- Michael additions and related vinylogous carbonyl reactions



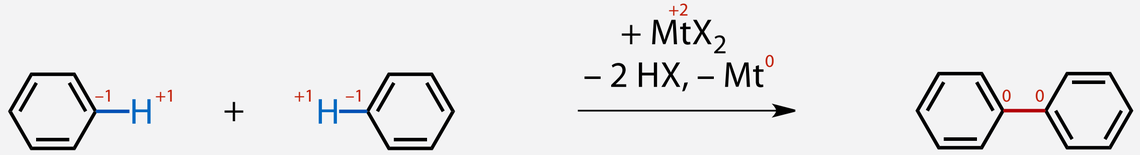
- Diels Alder reactions and related concerted cycloadditions



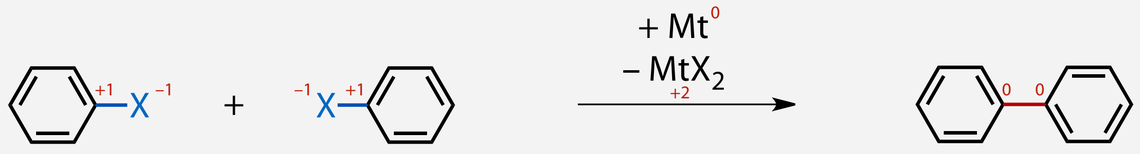
- **carbon bond forming reactions are an important branch of synthetic organic chemistry**

Organometallic Carbon Bond Forming Reactions

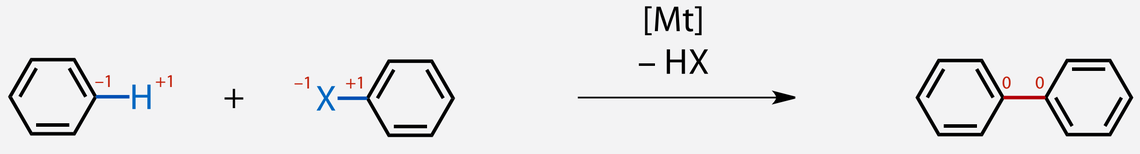
- oxidative homocoupling reactions



- reductive homocoupling reactions

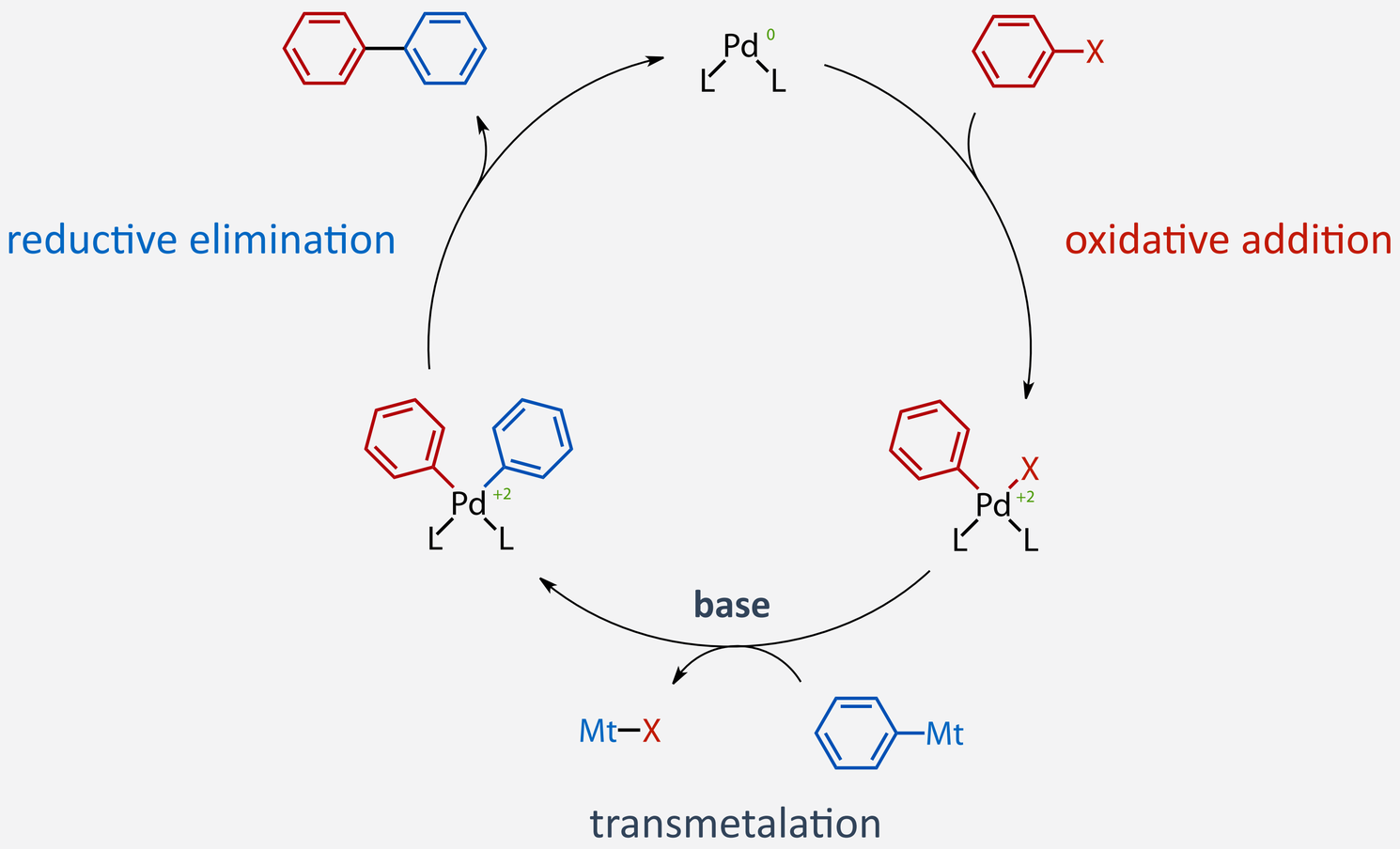


- catalytic cross-coupling reactions



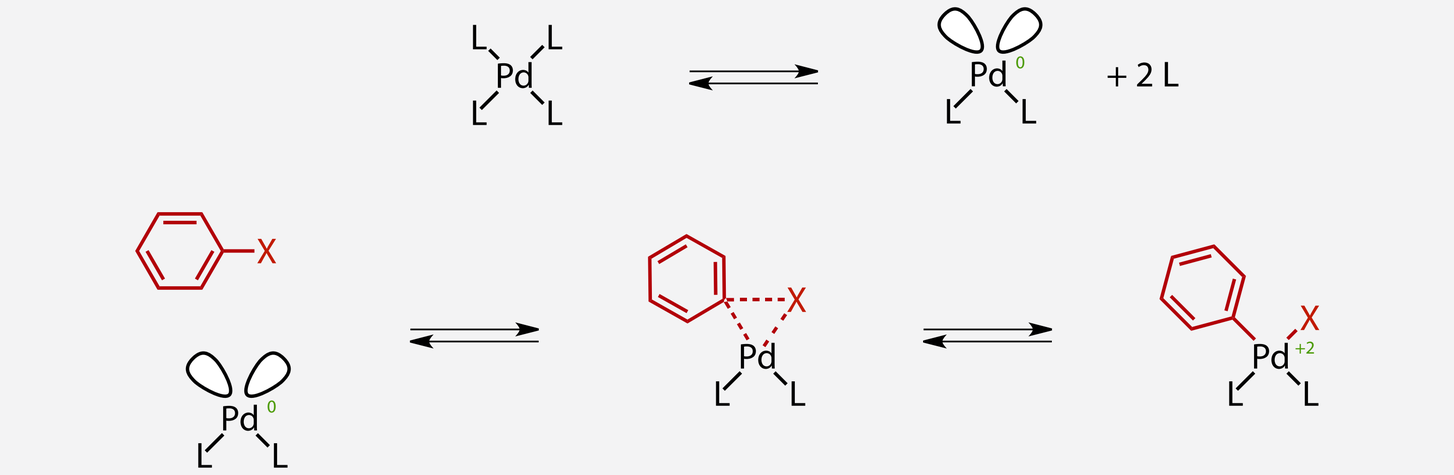
- **catalytic organometallic carbon bond forming reactions for organic semiconductor materials**

General Mechanism of Palladium-Catalyzed Cross-Coupling Reactions



- in a “cross-coupling” reaction, two different fragments R and R’ can be coupled together
- all steps in catalytic cycle are (usually) reversible, an exergonic step provides driving force

Ligand Dissociation and Oxidative Addition

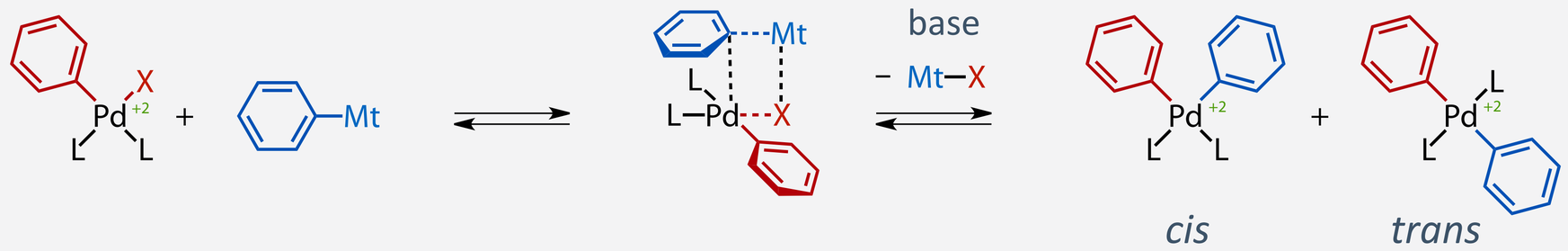


partially filled d orbitals | 4e3c bond | oxidized Pd center

- **metal center with partially filled, polarizable MO: transition metals (groups 3–12)**
- **metal center electron-rich & polarizable: “late” transition metals (groups 7–12)**
- **metal center with two stable oxidation states (difference +2): group 10 (Ni < Pd >> Pt)**

- **ligands L dissociable, making Pd electron-rich & polarizable, stabilizing molecular Pd^0**
- **ligands L strong σ-donors, moderate π-acceptors (phosphins PR_3, phosphinoxides $O{=}PR_3$)**
- **residue X electronegative, good leaving group, C–X bond weak: OTf ≈ I > Br >> Cl >>>F**

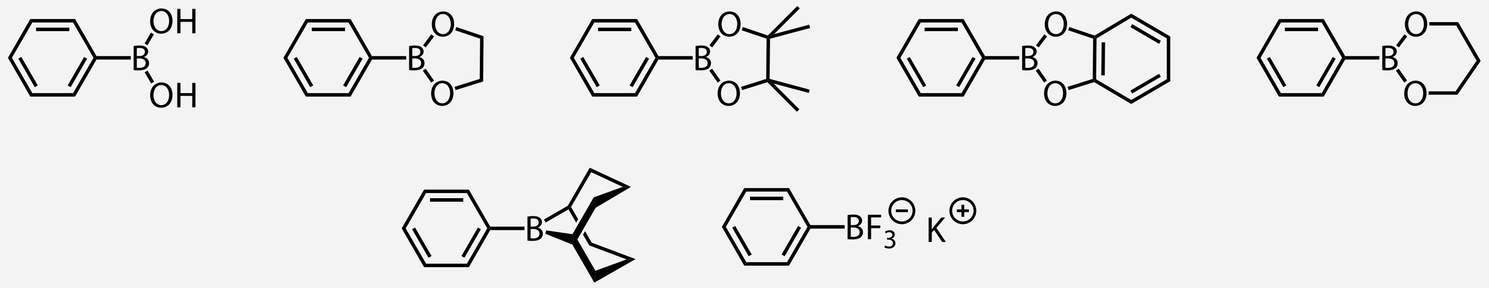
Transmetalation



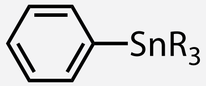
- metal center Mt is a main group metal (e.g. B, Si, Sn) or closed shell metal (e.g., Zn)
- formation of salts MtX or strong covalent bond Mt–X
- Pd^{2+} forms square-planar complexes, additional coordination sites for transmetalation
- *trans* addition preferred due to steric considerations (if not prohibited by “bridged” ligands)
- typical bases: Na_2CO_3, K_2CO_3, K_3PO_4, NaOH, NEt_3, pyridine, ...

Main Group Metals Used in Different Name Reactions

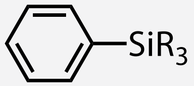
- Suzuki–Miyaura cross-coupling (requires a base)



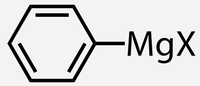
- Stille coupling



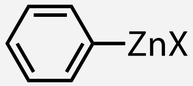
- Hiyama coupling



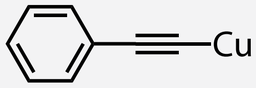
- Kumada coupling



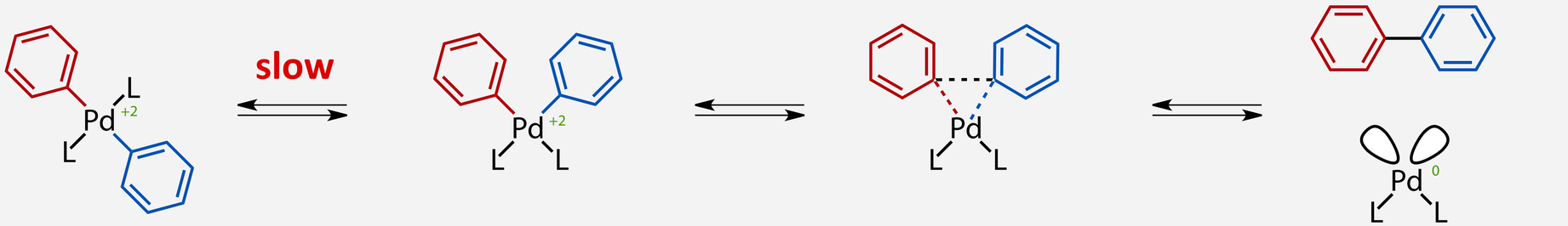
- Negishi coupling



- Sonogashira cross-coupling (requires a base)



Reductive Elimination

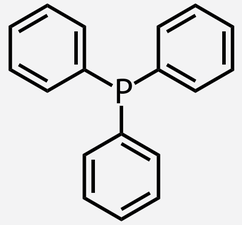


trans *cis* 4e3c bond reduced Pd center

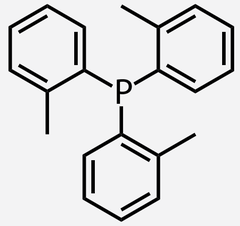
- reductive elimination only possible from ***cis*** stereoisomer
- ***cis-trans*** isomerization very slow
- ligands L should prohibit formation of ***trans*** isomer (bridged, bidentate L–L ligands)
- sterically demanding ligands L promote reductive elimination (“pushing out” the product)
- Pd center not too electron-rich, and well polarizable

Typical Catalysts and Ligands

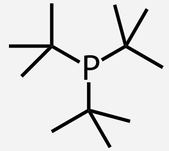
- monodentate ligands:



triphenylphosphine (PPh_3)

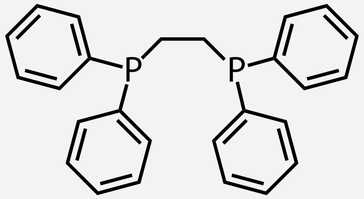


tri(*ortho*-tolyl)phosphine ($Ptol_3$)

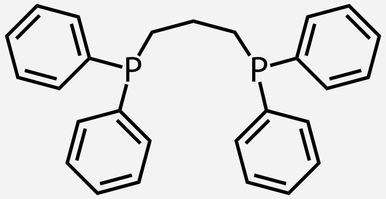


tri(*tert.*-butyl)phosphine (P^tBu_3)

- bidentate, bridged ligands (chelating ligands):



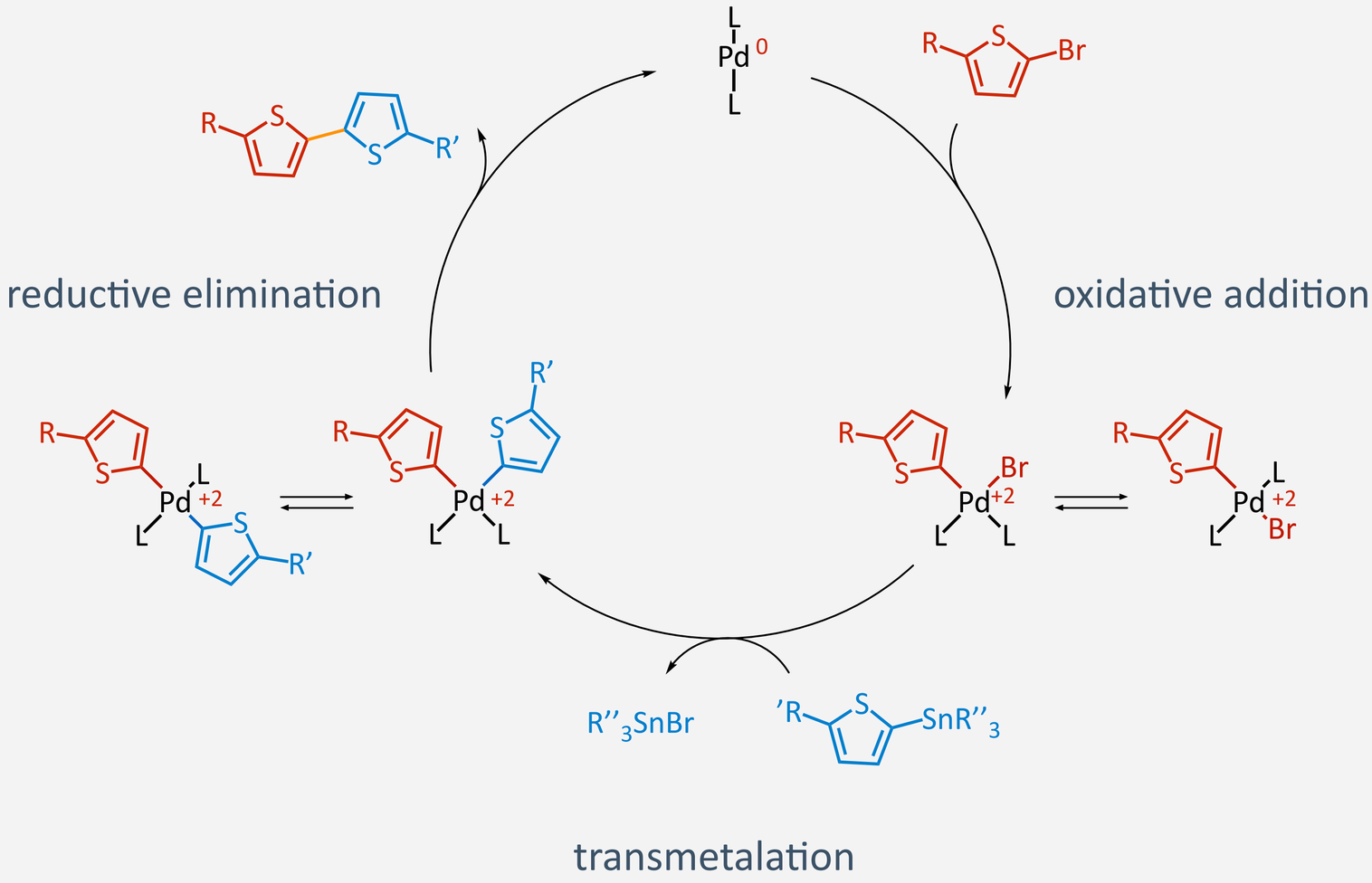
bis(diphenylphosphino)ethane (dppe)



bis(diphenylphosphino)propane (dppp)

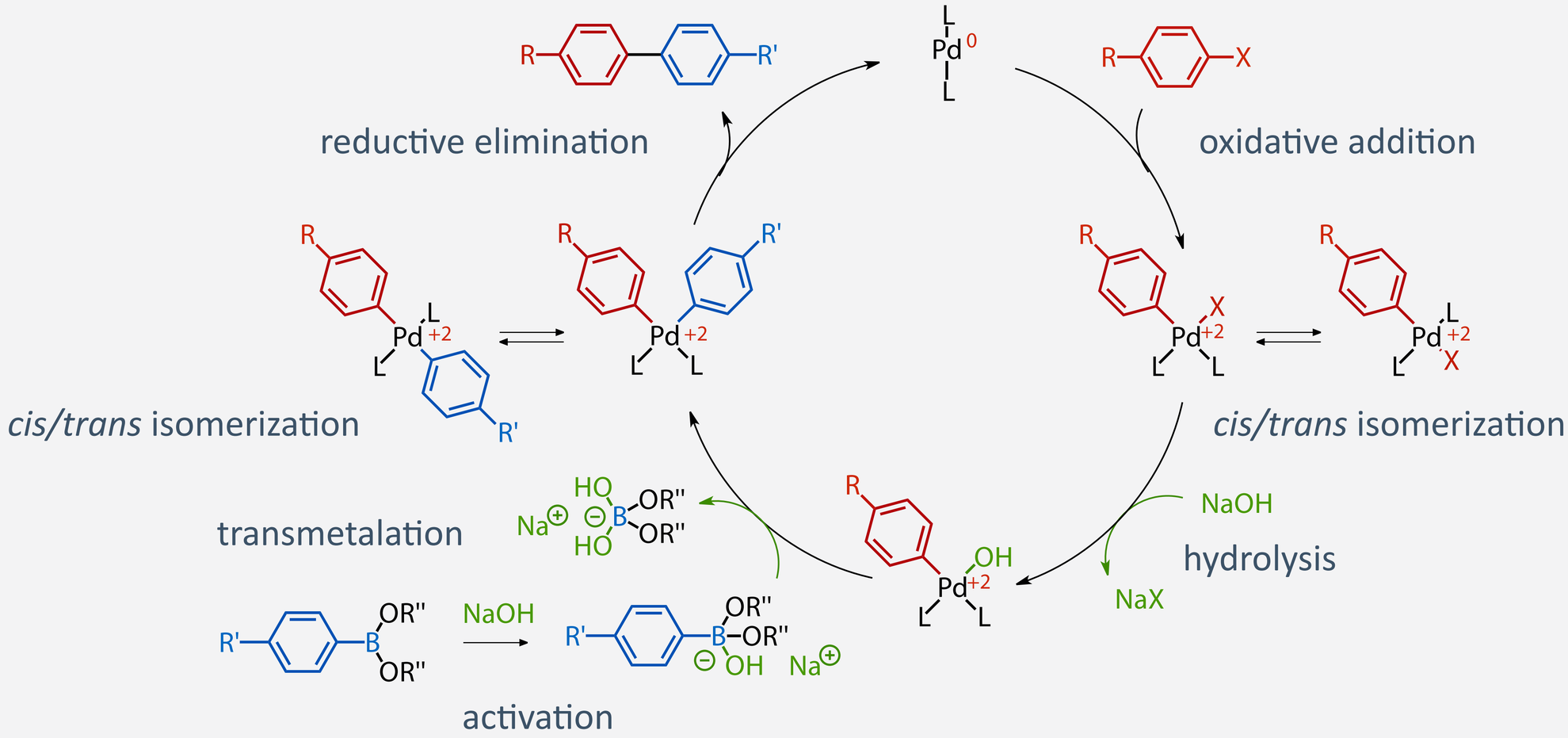
- **typical catalysts: $Pd(PPh_3)_4$, $Pd(Ptol_3)_4$, $Pd(P^tBu_3)_4$, $PdCl_2(PPh_3)_2$, $PdCl_2$(dppe), $PdCl_2$(dppp)**

Mechanism of the Stille Cross-Coupling Reaction



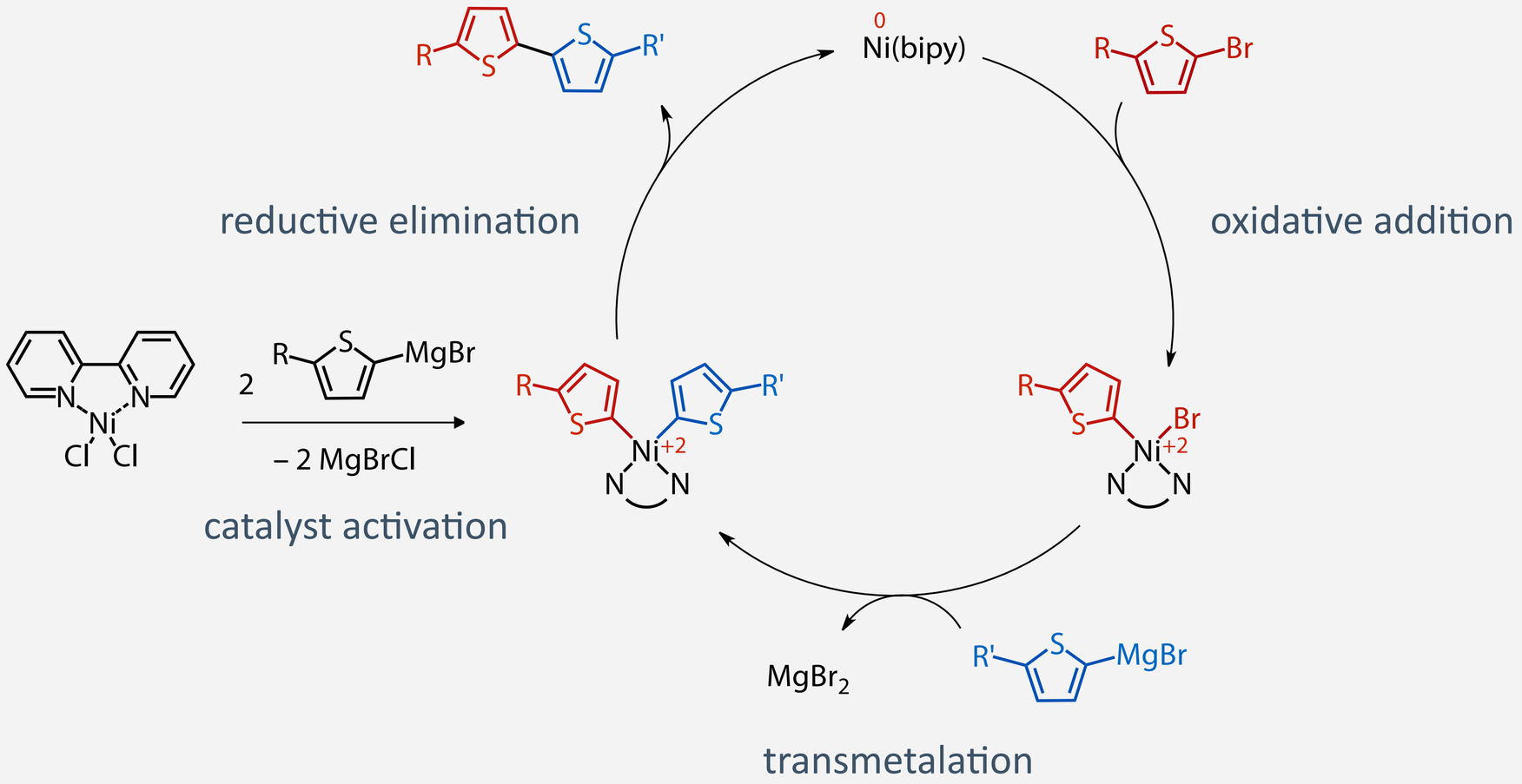
- **very benign conditions, no base, but organotin reagents are volatile, toxic, cancerogenic**

Mechanism of the Suzuki-Miyaura Cross-Coupling Reaction



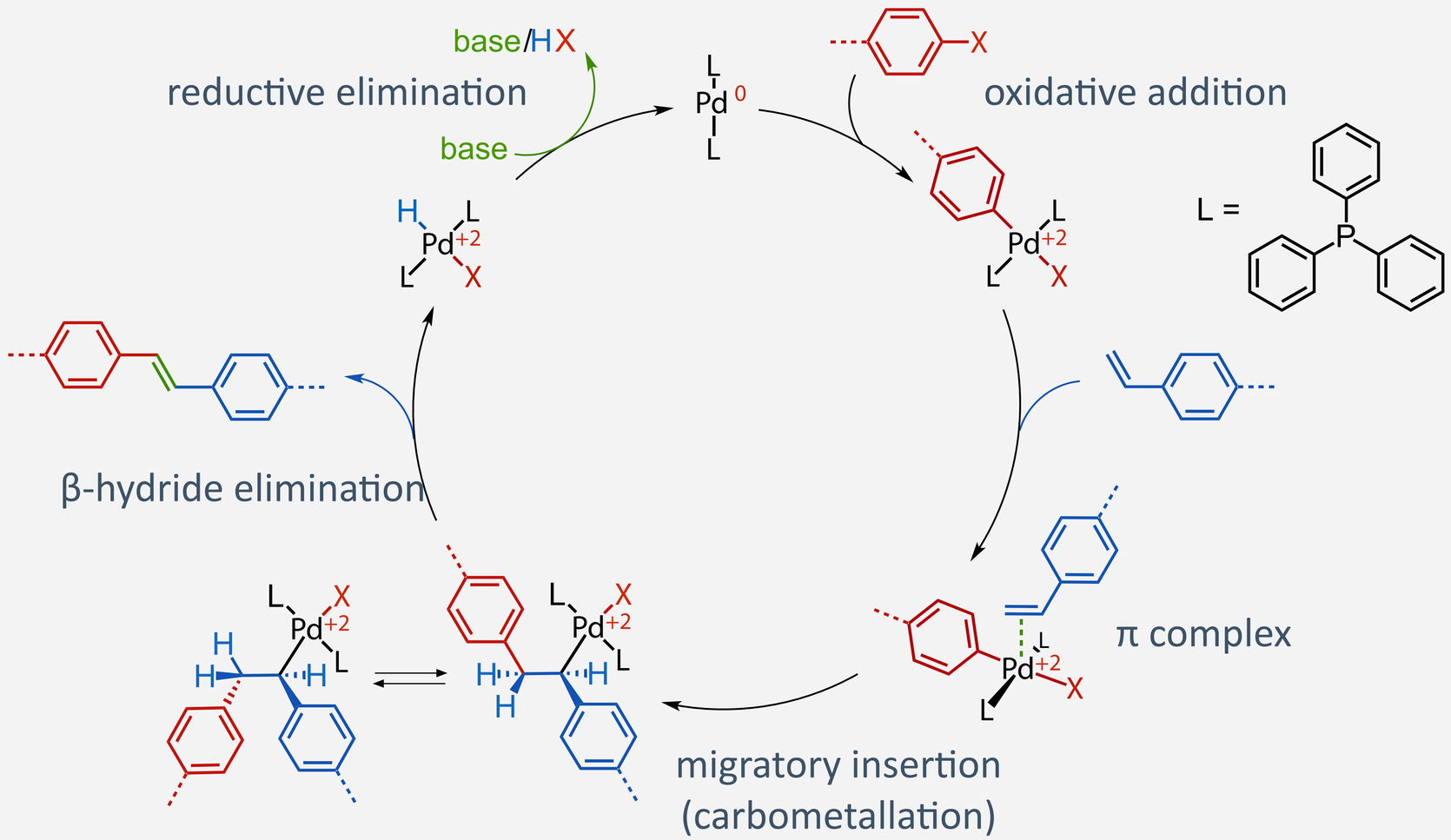
- **base mainly serves to activate the boronic acid derivative for the transmetalation step**

Proposed Mechanism of the Kumada Cross-Coupling



- **typically performed with Ni(II) catalyst, first activation by reduction with Grignard reagent**

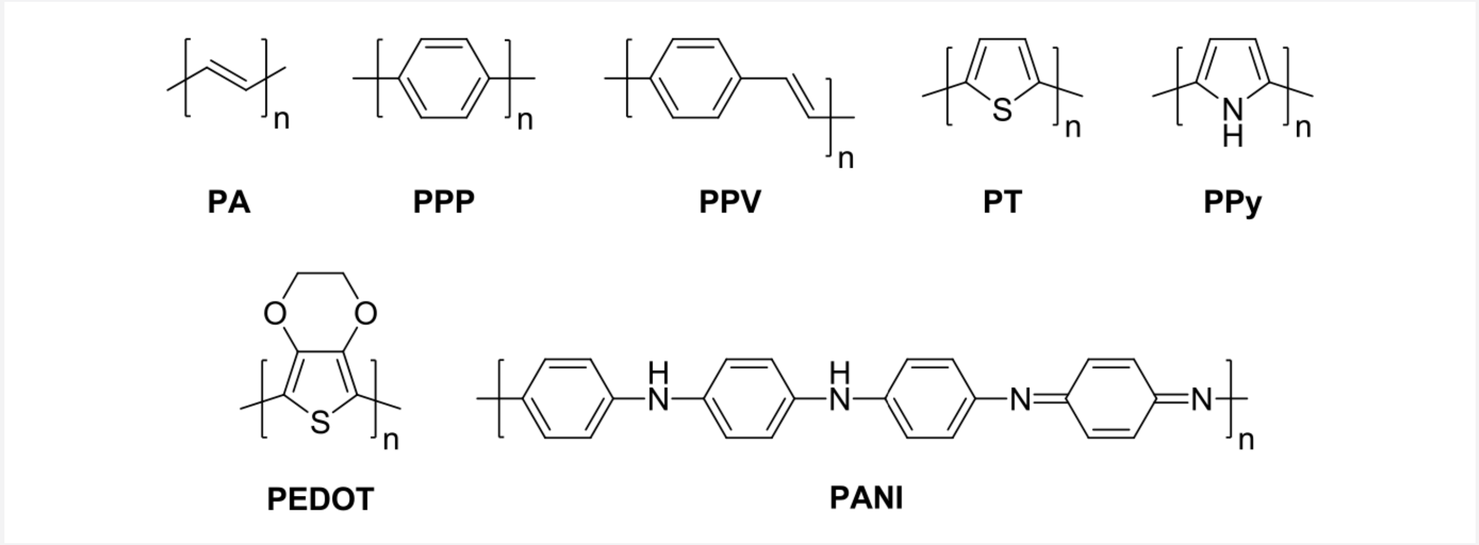
Proposed Mechanism of the Mizoroki-Heck Cross-Coupling Reaction



- **The Pd(0) complex must be regenerated from the Pd(II) product of β-elimination**

Linear Oligomers and Polymers

Typical Classes of Polymer Semiconductors



Dependence of Molecular Weight on Conversion and Stoichiometry

$$\overline{P_n} = \frac{1+r}{1+r-2x_p r}$$

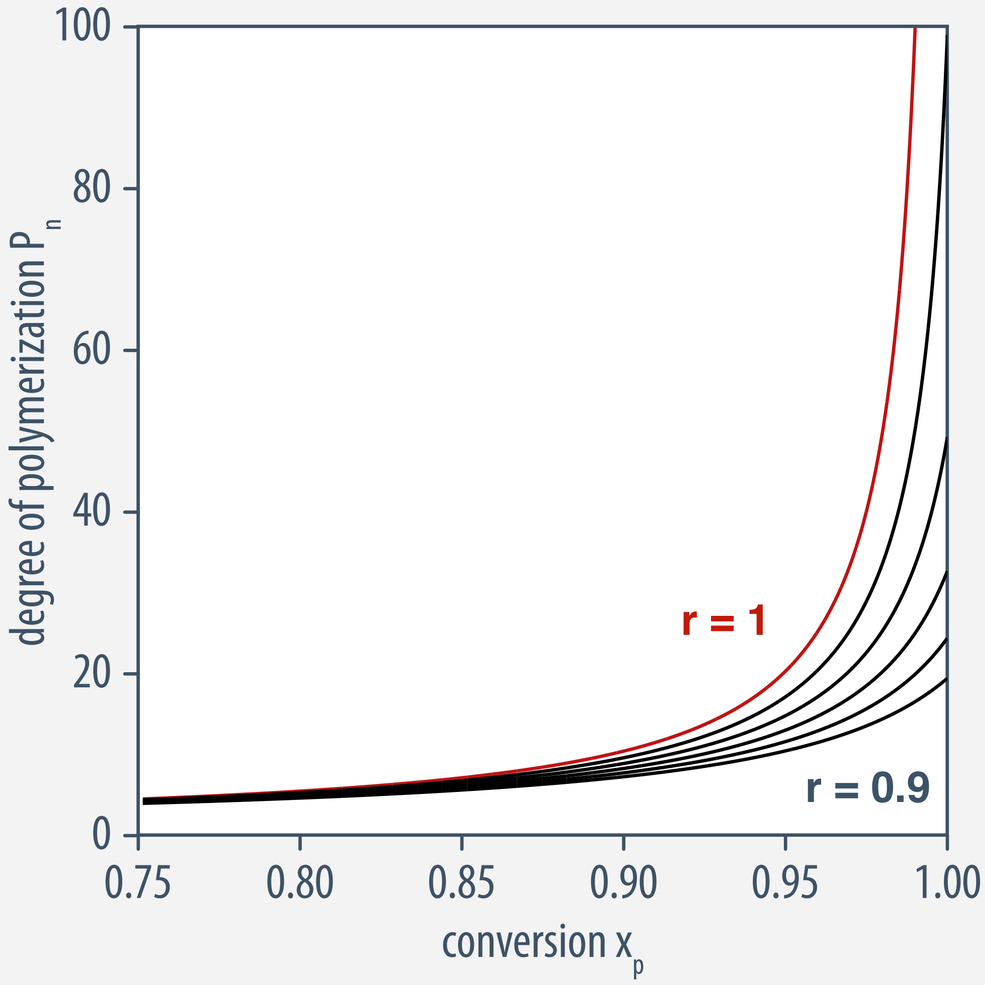
Carothers Equation

$$\overline{P_n} = \frac{1+r}{1-r}$$

for complete conversion ($x_p = 1$)

$$\overline{P_n} = \frac{1}{1-x_p}$$

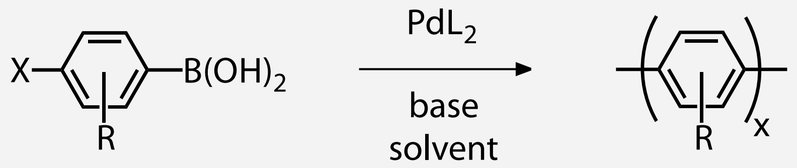
for perfect stoichiometry (r = 1)



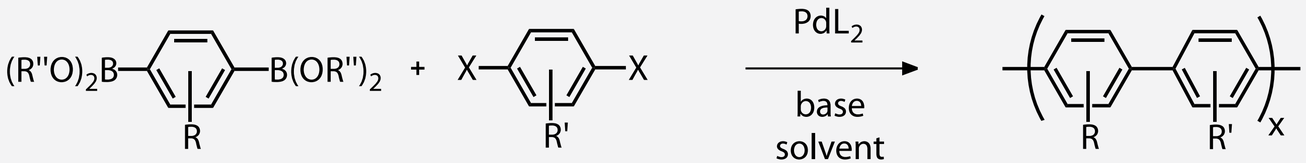
- **perfect stoichiometry, and very high conversion ($x_p > 0.99$) required for polymerization**

Suzuki Polycondensation

- poly(phenylene)s by Suzuki-Miyaura polycondensation (Schlüter et al.)



“AB monomer”



“AA monomer” “BB monomer”

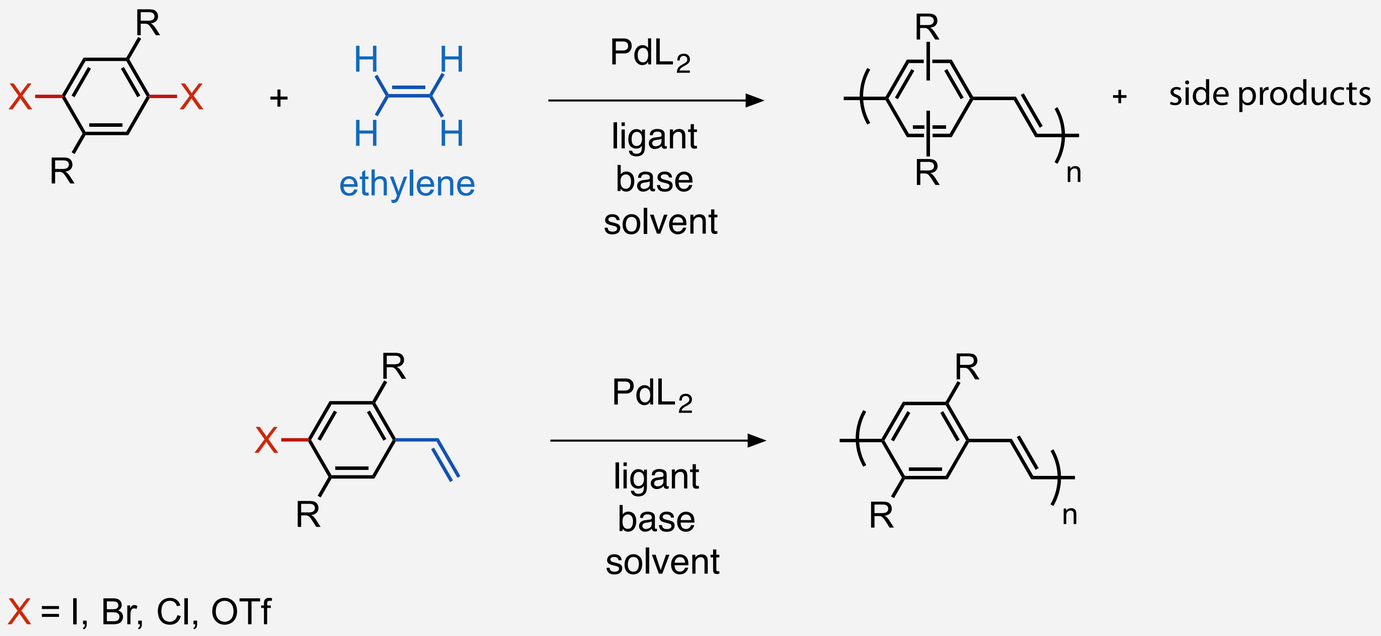
X = I, Br, Cl, OTf
R, R’ =H, alkyl, alkoxy

- **boronic acid derivatives are non-toxic, easy to prepare, stable compounds**
- **mild reaction conditions; tolerant towards functional groups, solvents, air; chemoselective**
- **often performed in toluene/water mixtures (driving force from Mt–X transfer into water)**
- **alkyl decoration of the rigid polymer backbone for improved (entropy-driven) solubility**

A. D. Schlüter, *J. Polym. Sci. Part A: Polym. Chem.* 2001, 39, 1533.

Mizoroki-Heck Cross-Coupling Reaction

- polymers using the Mizoroki-Heck cross-coupling reaction:

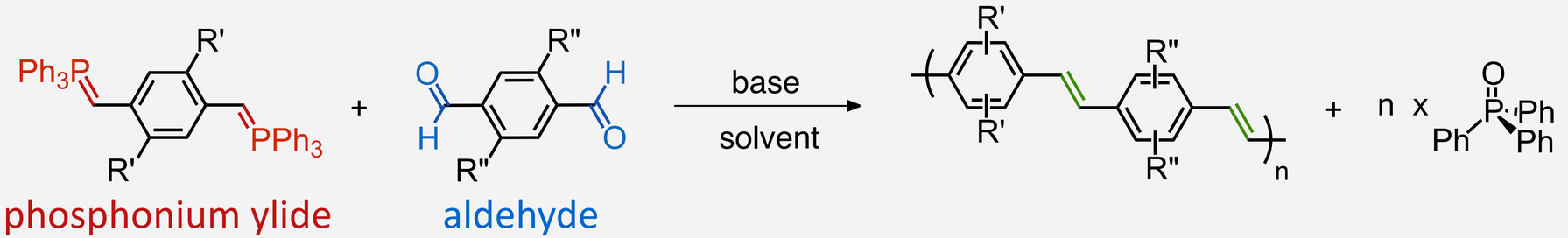


- **vinyl bonds only in the *trans* configuration**
- **high molecular weights depending on solubilizing groups**

Y. Li et al., *J. Polym. Sci. Part A: Polym. Chem.* 2006, *44*, 1279

Wittig Olefination Reaction

- polymers using the Wittig cross-coupling reaction:

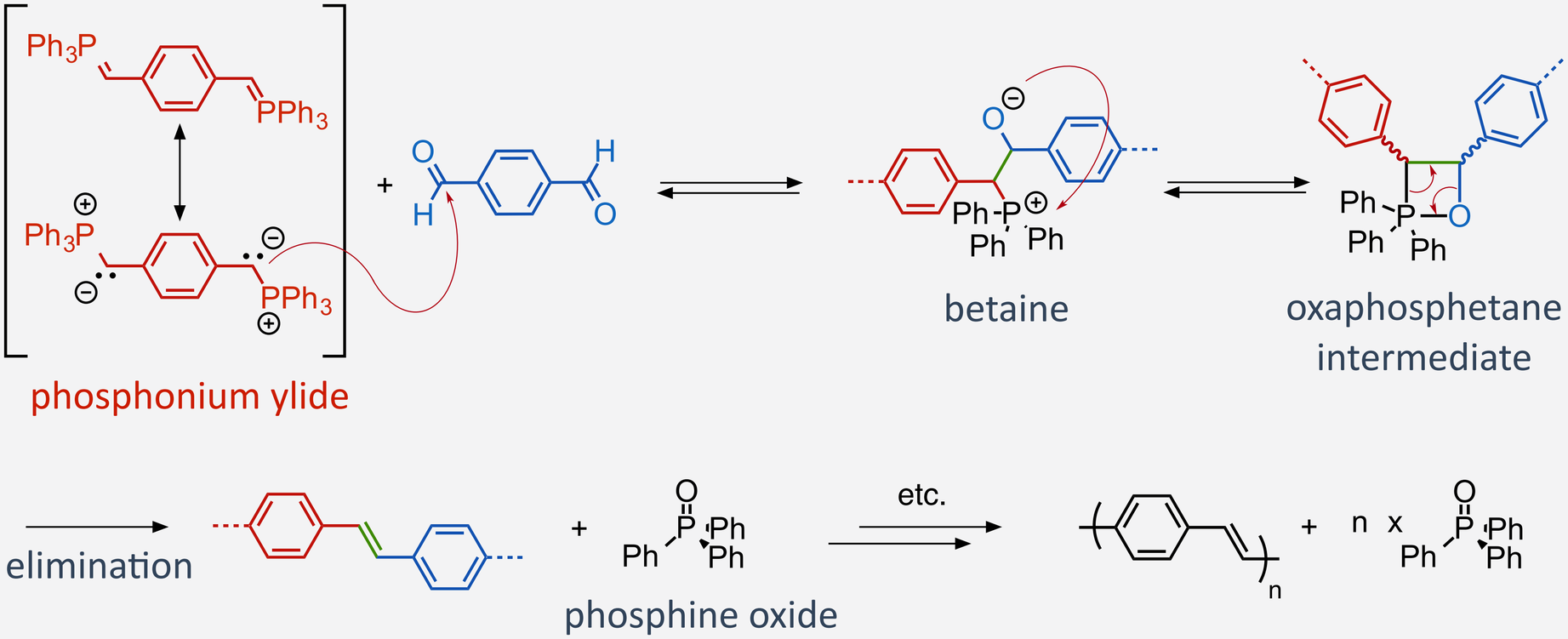


- **vinyl bonds in *cis* and *trans* conformation based on the ylide side groups**
- **incorporation of various side groups (alkyl, alkoxy, or phenyl)**

A. Drury et al., *Synth. Met.* **1999**, 103, 2478

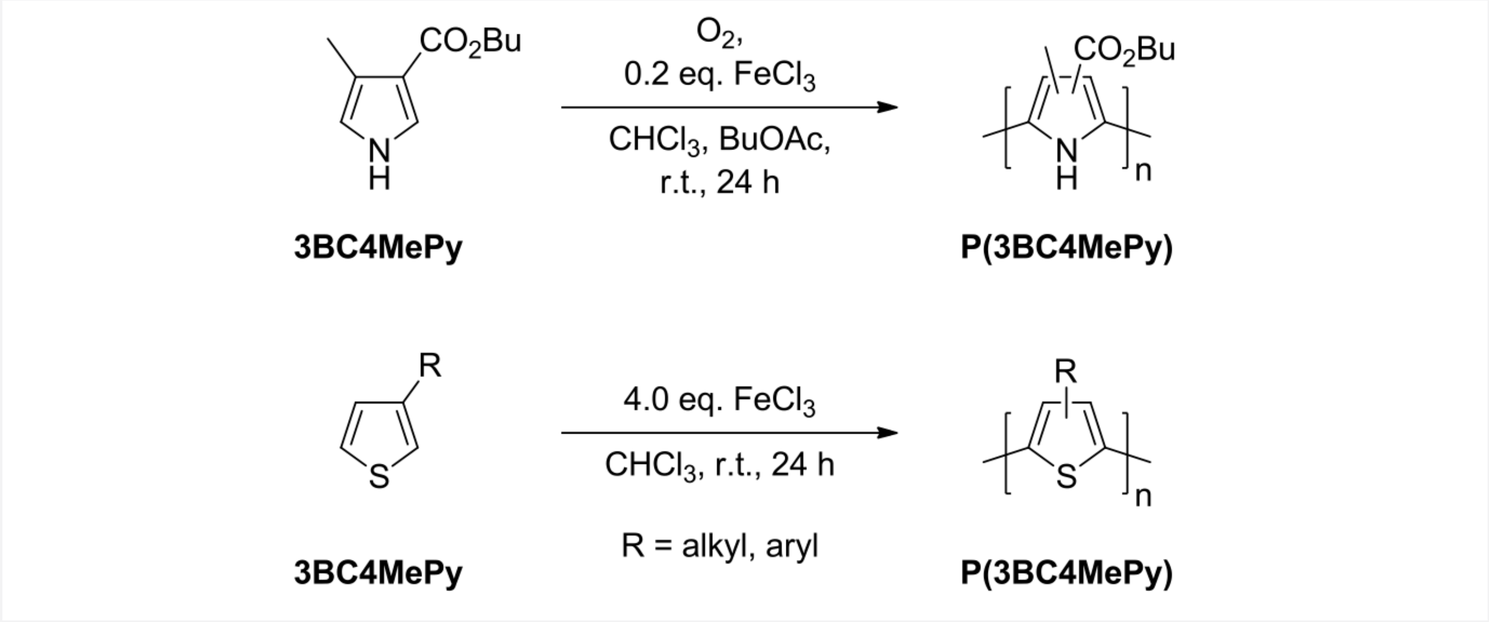
Mechanism of the Wittig Olefination Reaction

- proposed mechanism of the Wittig polycondensation:



- **ring decomposition is the rate-determining step**
- **stabilized ylides result in almost exclusive formation of the *E*-alkene product (*trans* isomer)**

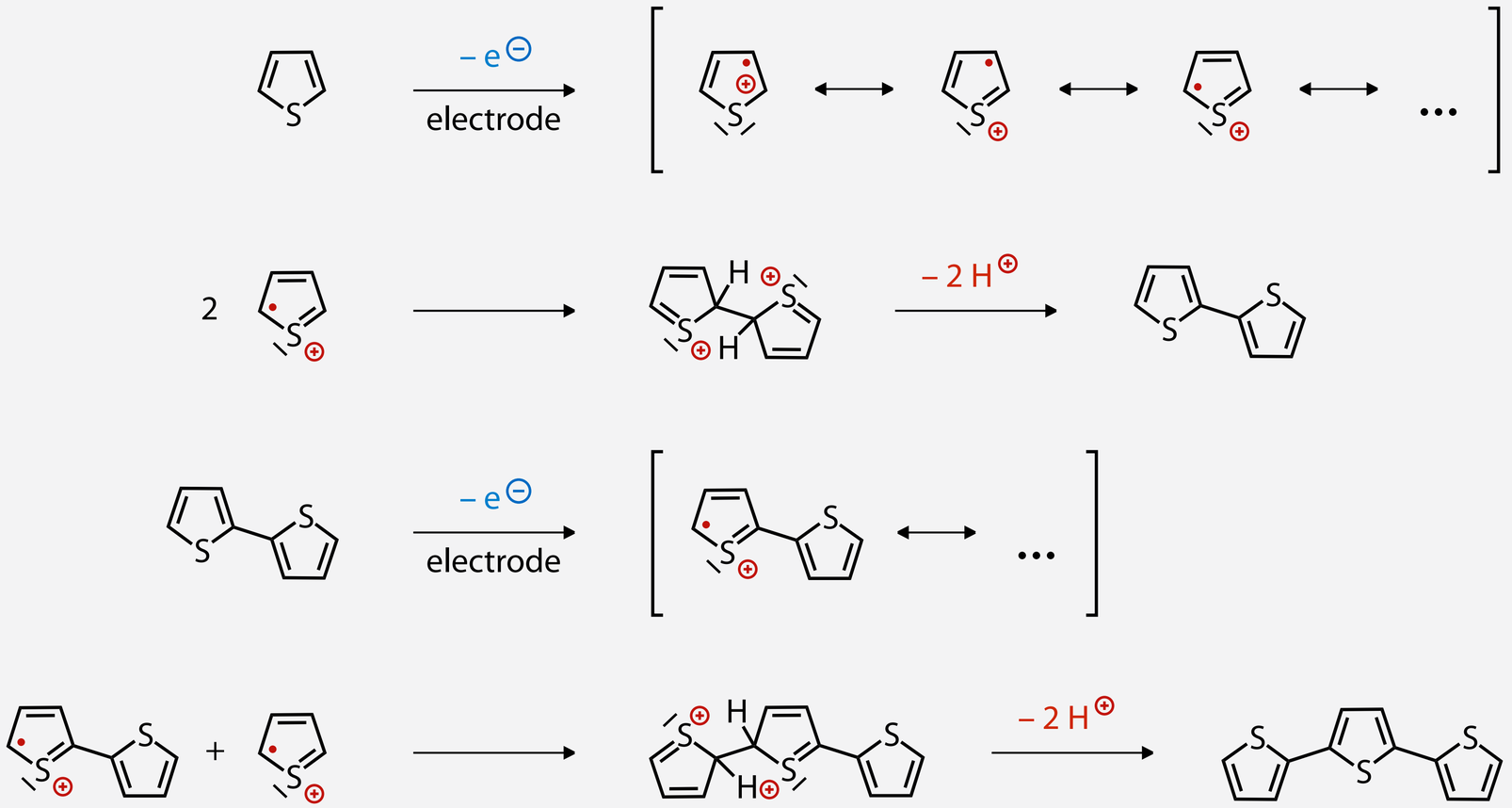
Oxidative Polymerization of Pyrrole and Thiophene Derivatives



- simple polymerization procedures with catalytic or superstoichiometric amounts of oxidant
- can also be performed electrochemically diretcly on an electrode

Electrochemical Polymerization of Thiophene

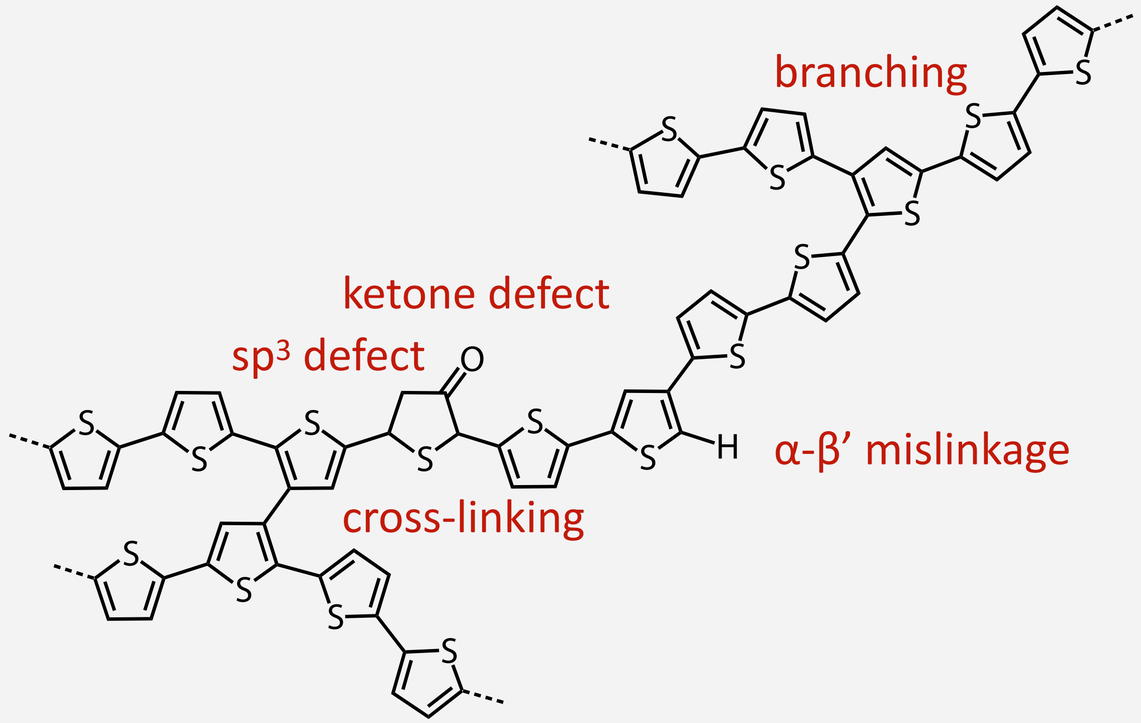
- proposed mechanism of the electrochemical thiophene polymerization:



- **due to increasingly low solubility, obtained poly(thiophene) will have low molecular weight**

J. Simitzis et al., *J. Appl. Polym. Sci.* **2010**, *118*, 1494

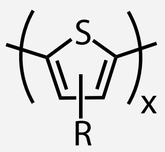
Electrochemical Polymerization of Thiophene

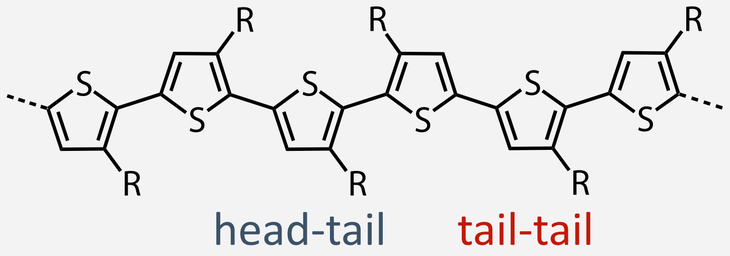


- polymerization directly on an anode, in monomer solution
- no solubility or purification problems during synthesis, no catalyst required
- obtained poly(thiophene) is spontaneously p-doped, but also contains numerous defects.

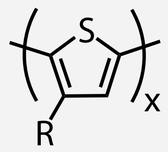
Regioregularity of Poly(3-alkylthiophene)s

irregular poly(alkylthiophene)





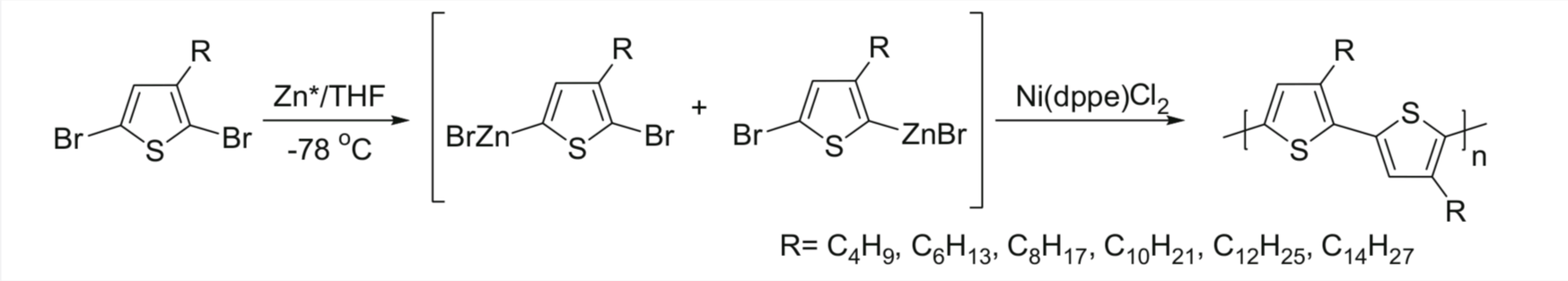
regioregular poly(3-alkylthiophene)



- alkyl decoration yields soluble, processable poly(thiophene) derivatives
- possibility of regioisomers by “erroneous” connections (head-head, tail-tail)
- irregularities disturb geometry, reduce effective conjugation length
- regioregular poly(3-alkylthiophene)s show improved properties

Synthesis of Poly(Alkylthiophene)s

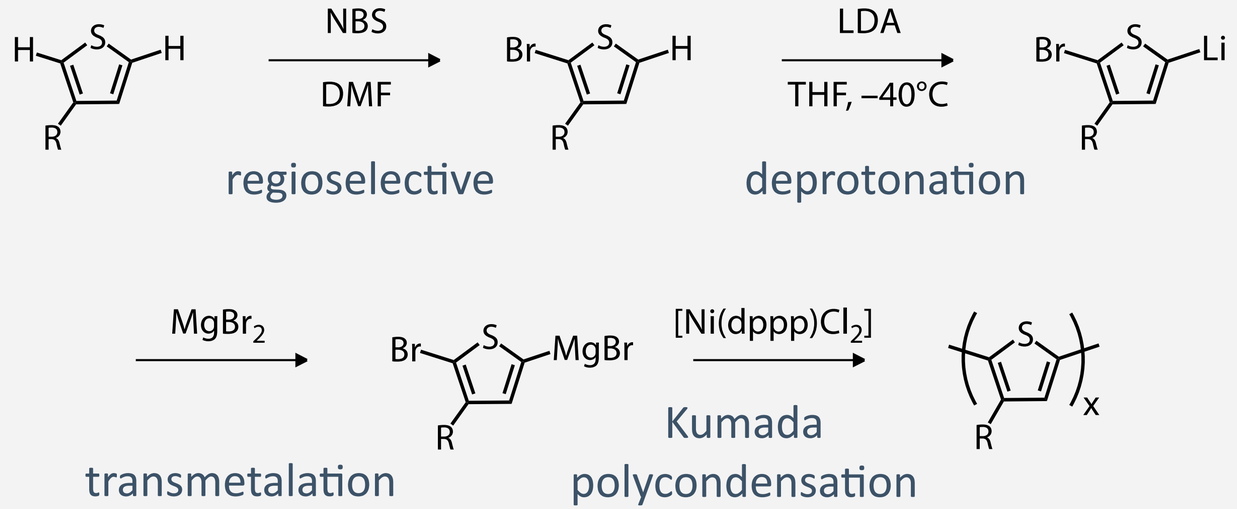
- Rieke methods for the synthesis of P3HT makes use of zinc Grignard reagent
- zinc Grignard reagent generated from arylbromide using Rieke zinc ($ZnCl_2$ + Li in situ)



- **symmetric monomer, statistical reaction gives rise to regio-irregular poly(alkylthiophene)s**
- **regioregularity needed to control packing in crystalline state and thus increase mobility**

Synthesis of Regioregular Poly(3-alkylthiophene)s

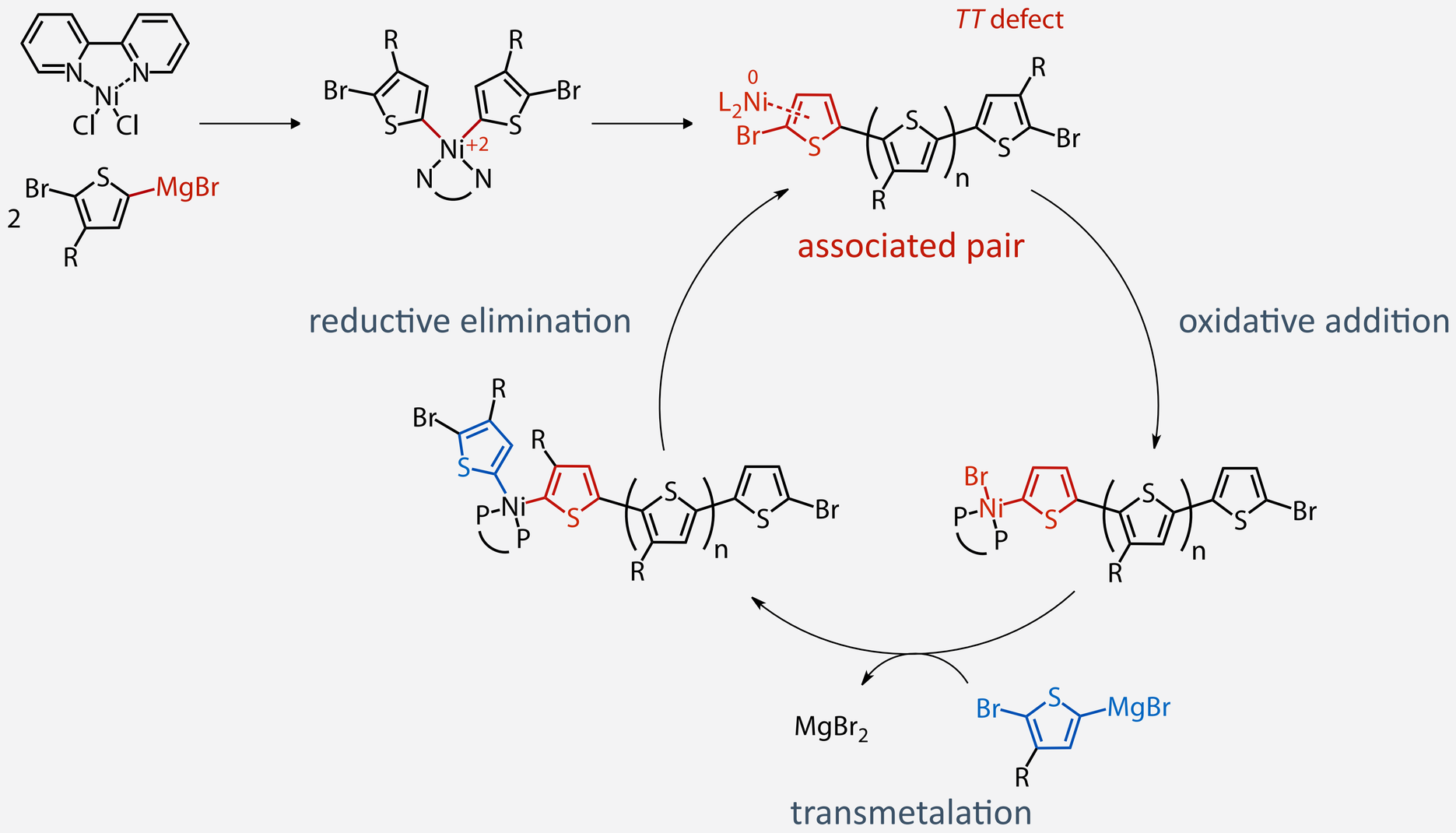
- McCullough Route: first synthesis of regioregular P3AT via Kumada polycondensation



- **regioselectivity due to selective bromination and lithiation by deprotonation**
- **lithiated thiophene stable at –40°C, does not react with bromide**
- **obtained poly(3-alkylthiophene) is 91% regioregular**
- **certain features of a living polymerization (controlled MW, narrow MWD, low PDI)**

R. D. McCullough et al., *J. Chem. Soc., Chem Commun.* **1992**, 70

Mechanism of the Kumada Polycondensation According to McCullough



- **Ni catalyst like initiator, remains at chain end, preferential oxidative addition of chain end**

R. D. McCullough et al., *Macromolecules* **2004**, 3526

Structure and Properties of Poly(thiophene)s

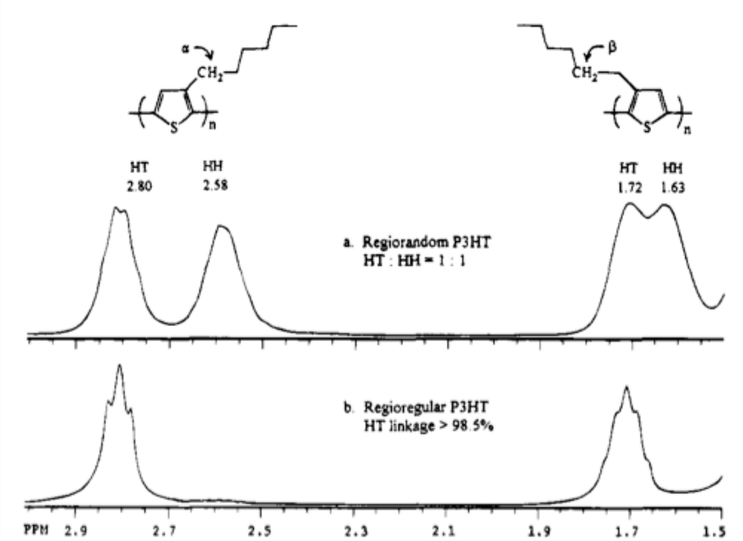


Figure 2. Expanded ^{1}H NMR spectra of (a) regiorandom P3HT **5b** (1:1 HT/HH) and (b) regioregular P3HT **4b** (HT linkage >98.5%).

	McCullough	Rieke	$FeCl_3$
HT-HT (%)	91	54	54
HT-HH (%)	5	17	13
TT-HT (%)	2	13	18
TT-HH (%)	2	16	15
UV-Vis λ_{max} (nm)	450	428	436
conductivity (S/cm)	600	n.d.	10
mobility ($cm^2/(V{\cdot}s)$	10^{-1}	n.d.	10^{-5}

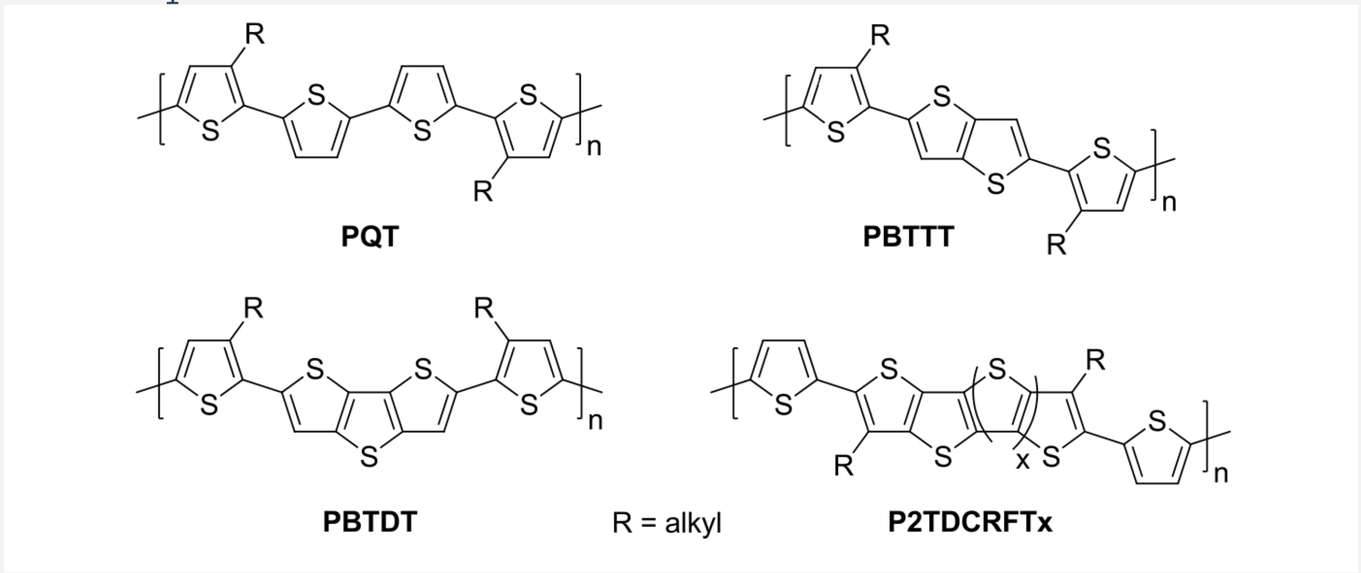
- **alkyl defects reduce effective conjugation length and disturb crystalline domains**
- **band gap increased, mobility and conductivity decreased**

McCulloch, Chem. Mater. **2014**, *26*, 647–663

Polymer Structure and Air Stability

HOMO –4.9 eV
$\mu = 0.14\ cm^2\ V^{-1}\ s^{-1}$

HOMO –5.1 eV
$\mu = 0.2\ cm^2\ V^{-1}\ s^{-1}$



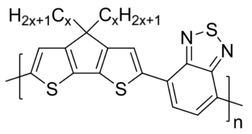
HOMO –5.2 eV
$\mu \leq 0.0017\ cm^2\ V^{-1}\ s^{-1}$

HOMO –5.3 eV
$\mu \leq 0.087\ cm^2\ V^{-1}\ s^{-1}$

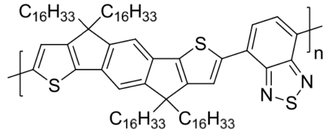
- **incorporation of fused thiophene systems decreases HOMO level and increases air stability**
- **however, mobility decreased (probably due to reduced microstructural order)**

Malliaras, *J. Am. Chem. Soc.* **2009**, *131*, 11930

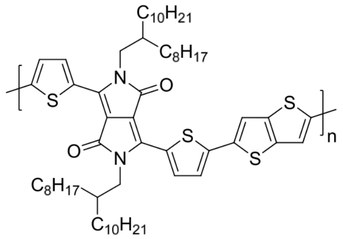
Donor-Acceptor (Low Bandgap) Polymers



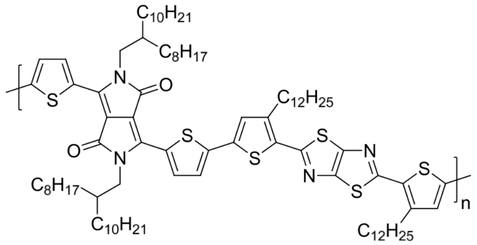
CDT-BTZ-Cx
(x = 16 or 20)



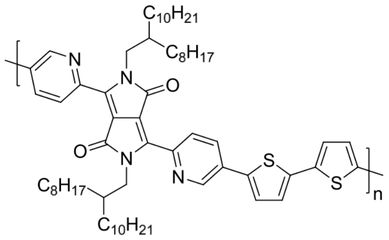
ID-BTZ



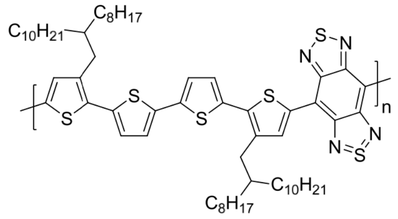
P(DPP2ODT2-TT)



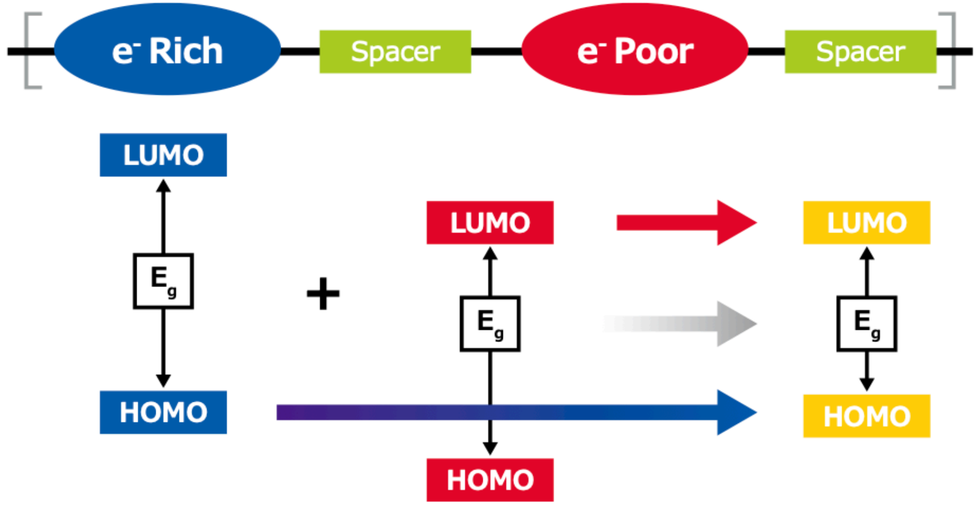
P(DPP2ODT2-TzBT12)



P(DPP2ODPy2-T2)



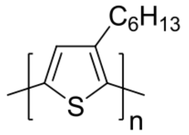
PBBTQT



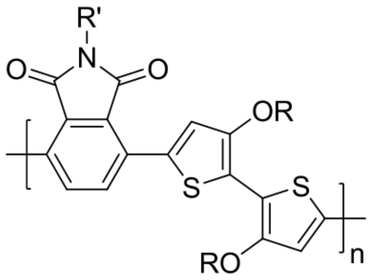
- combination of electron donor and acceptor units in the same π-conjugated polymer

Watson, J. *Am. Chem. Soc.* **2009**, 131, 7206

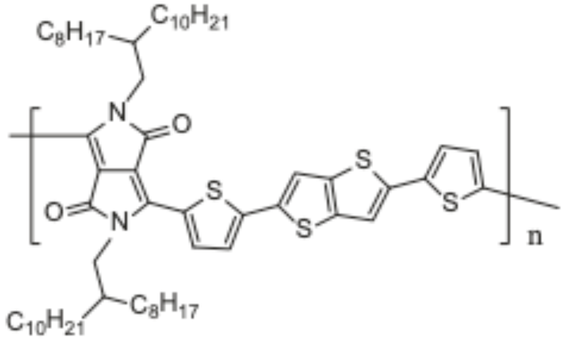
Donor-Acceptor (Low Bandgap) Polymers

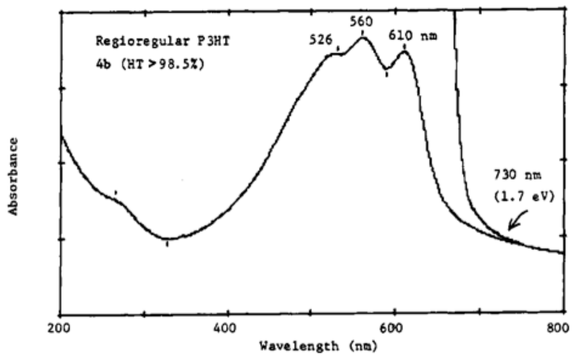


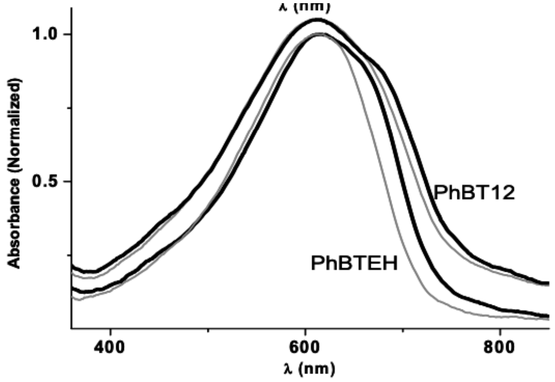
P3HT

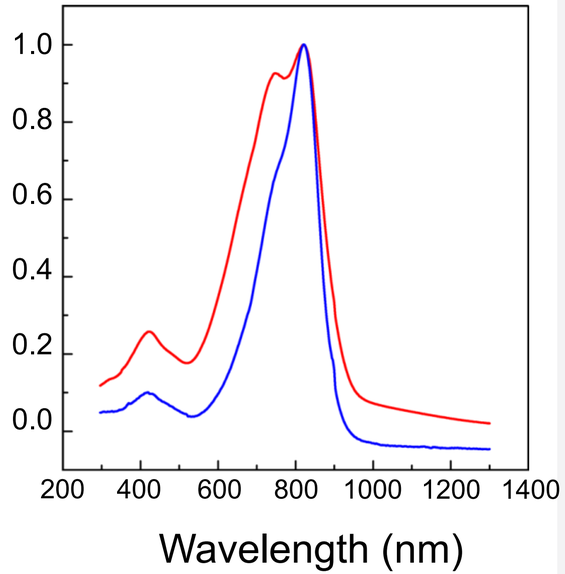


PhBTR







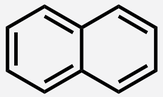


Watson, *J. Am. Chem. Soc.* **2009**, *131*, 7206; Ong, *Scientific Reports* **2012**, *2*, 754

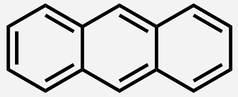
Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs)

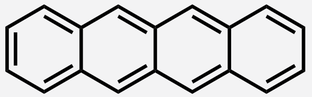
benzene



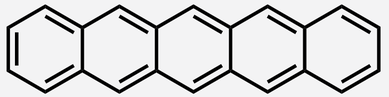
naphthalene



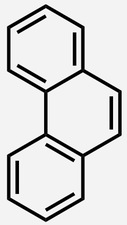
anthracene



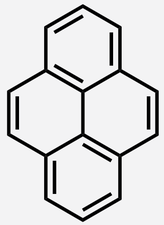
tetracene



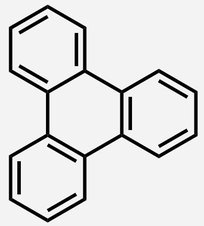
pentacene



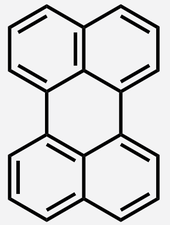
phenanthrene



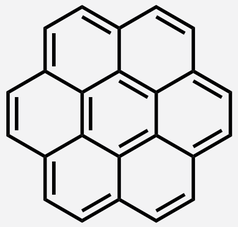
pyrene



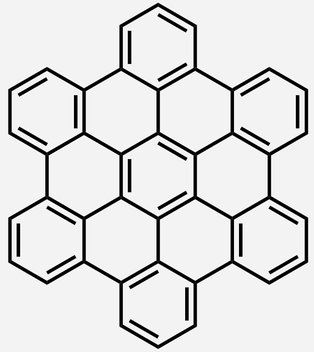
triphenylene



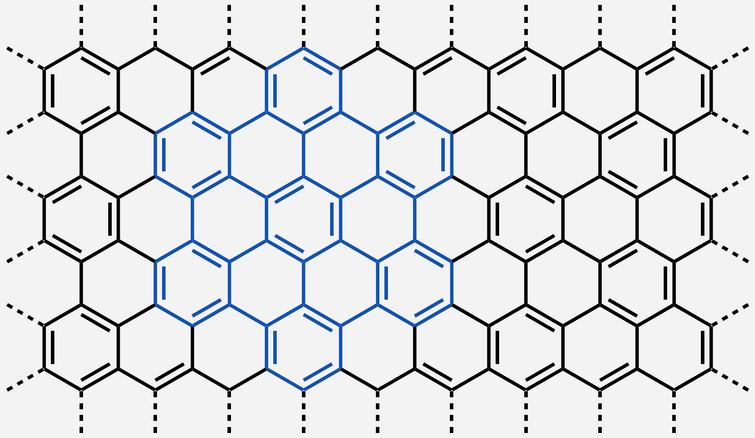
perylene



coronene

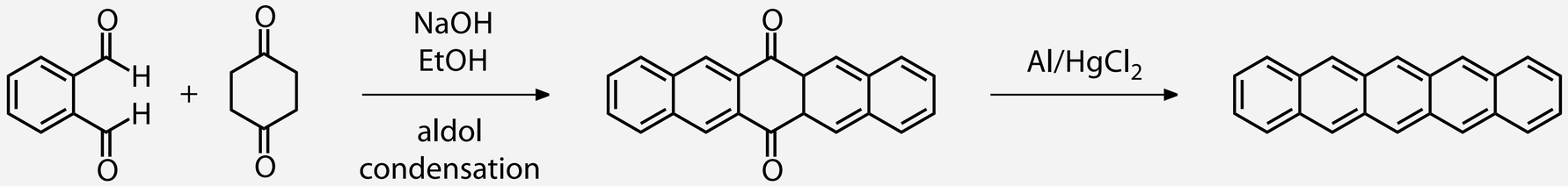


hexabenzocoronene

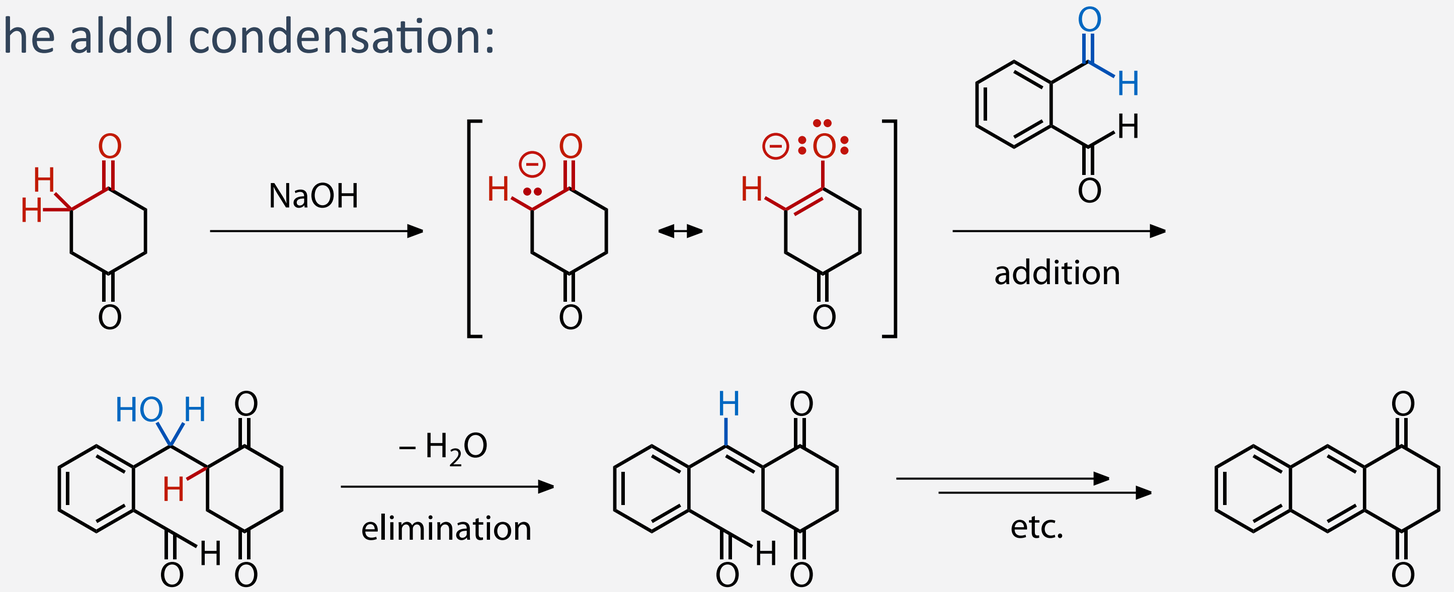


graphene

Synthesis of Pentacenes

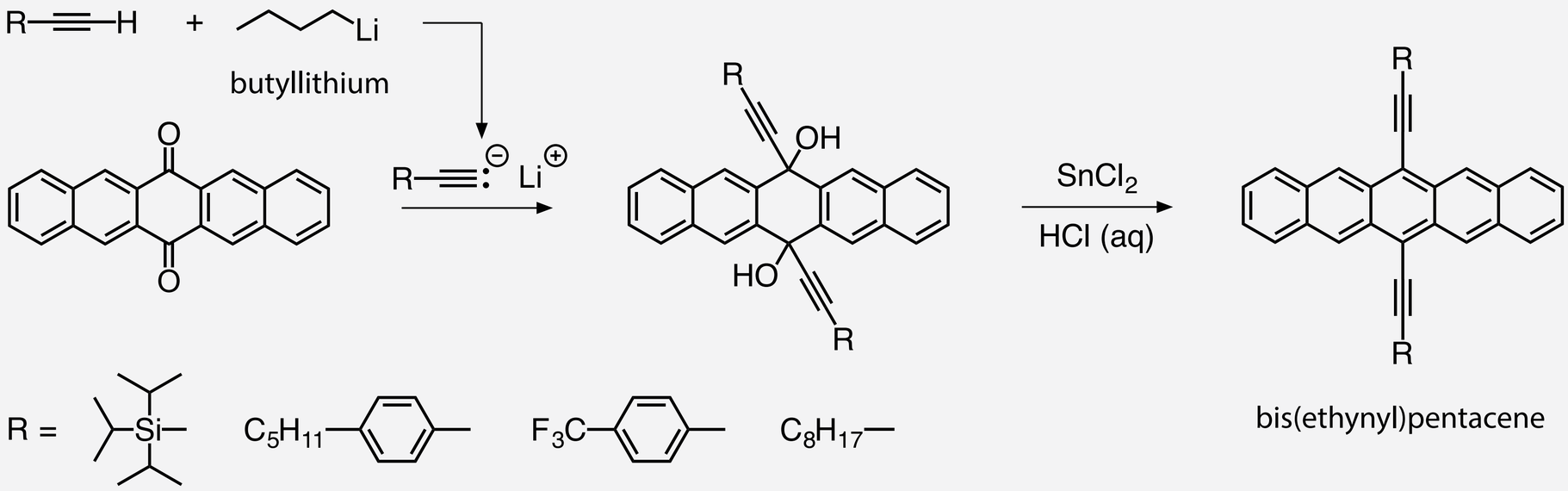


- mechanism of the aldol condensation:

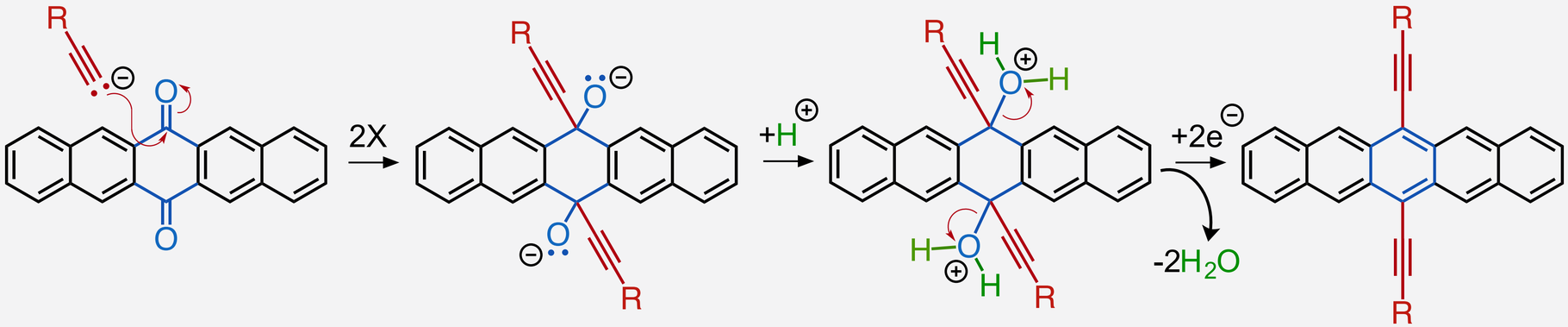


Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452

Synthesis of Soluble Pentacenes



- **mechanism of the nucleophilic attack on the "quinone" unit:**



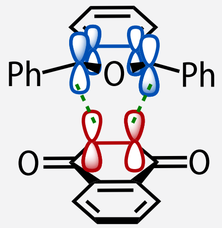
B. S. Ong, *Chem. Mater.* **2007**, *19*, 418

Frontier Orbital Participation in Diels Alder Reactions

- Diels Alder cycloadditions are “orbital-controlled” concerted reactions

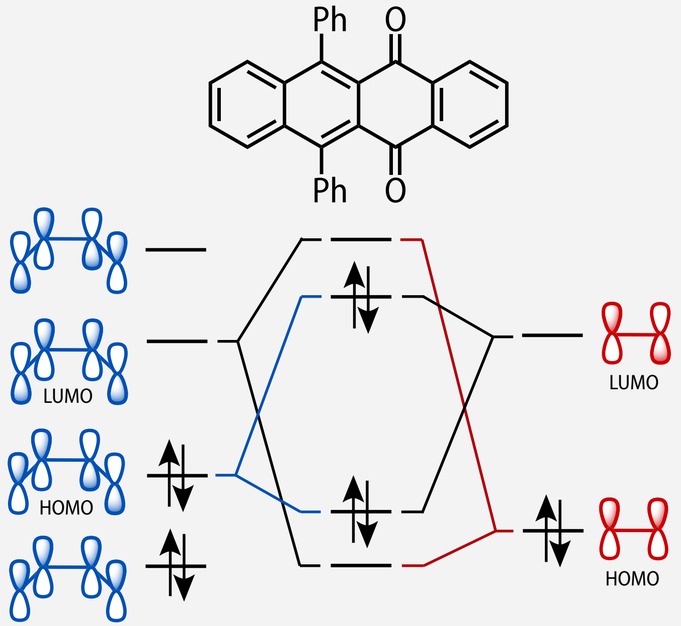
(electron-rich diene)

HOMO



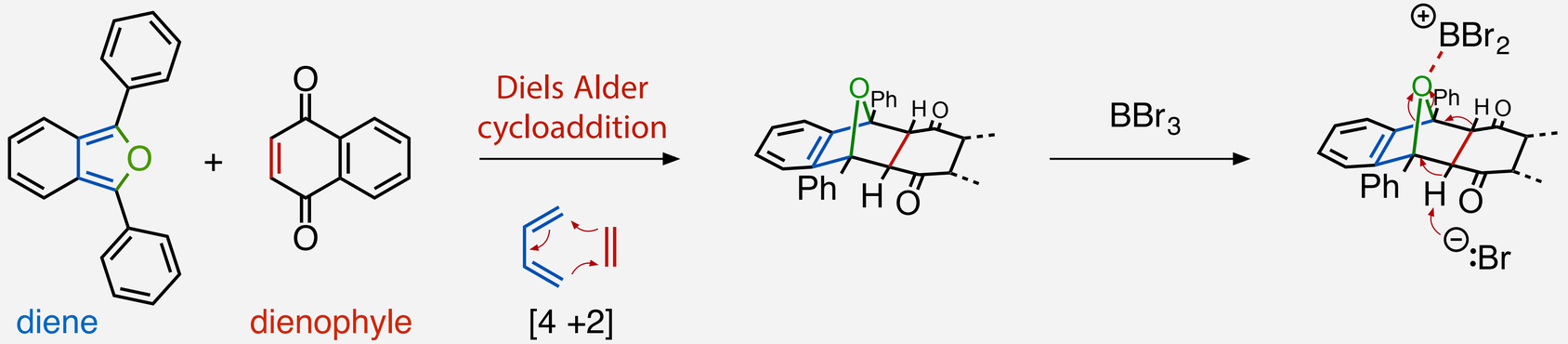
LUMO

(electron-deficient dienophile)



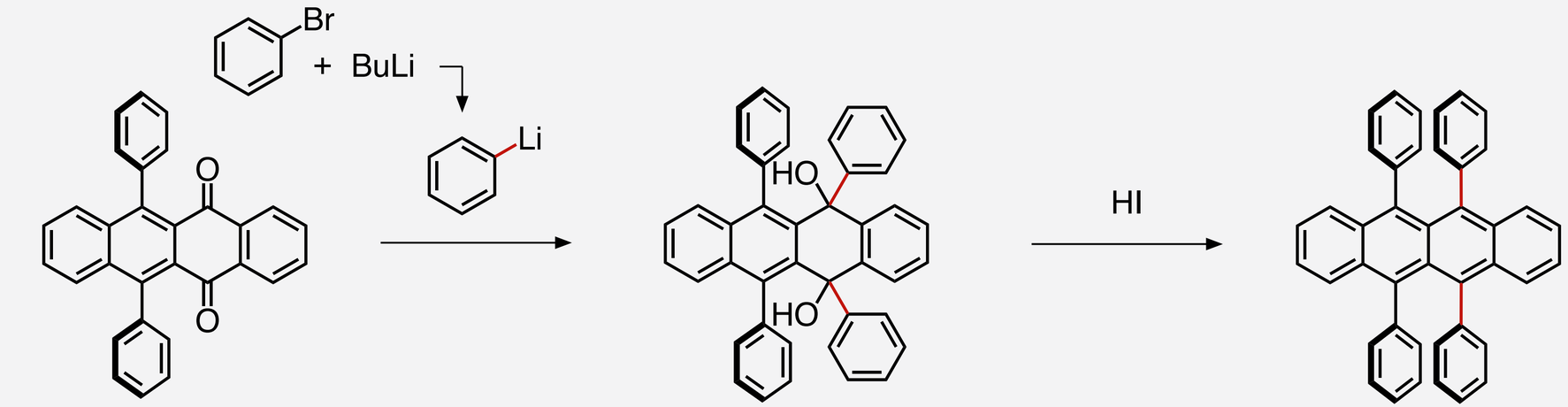
- **“normal electron demand” Diels Alder: electron-rich diene and electron-poor dienophile**
- **orbital overlap between HOMO of electron-rich diene and LUMO electron-poor dienophile**

Synthesis of Rubrene



diene

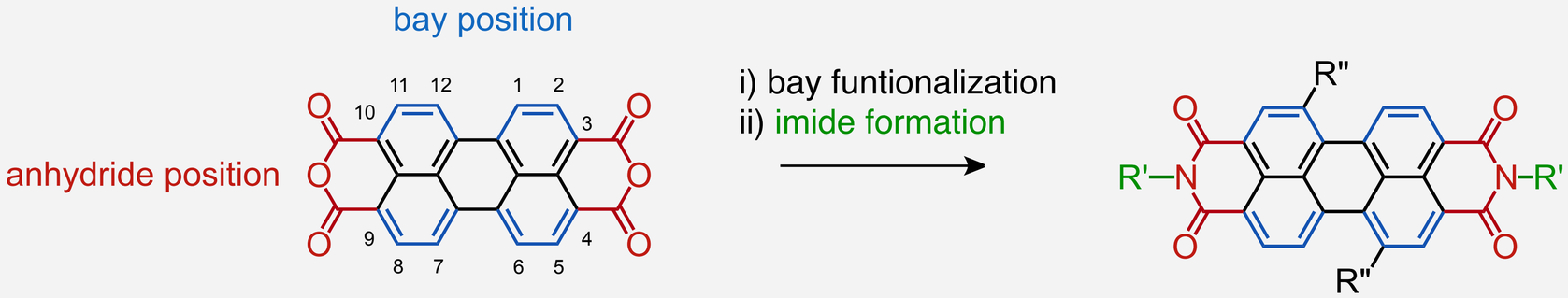
dienophyle



diphenyltetracenedione

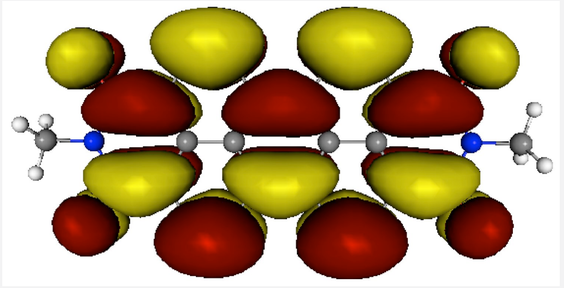
rubrene

Perylene Derivatives

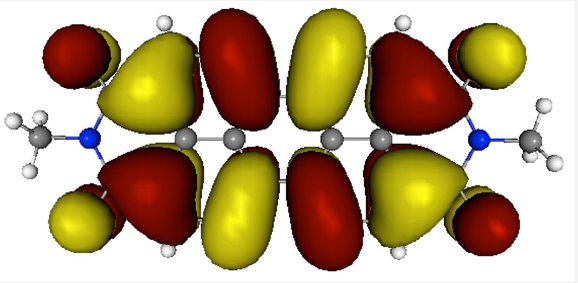


perylene-3,4,9,10-tetracarboxylic dianhydride

perylene diimide



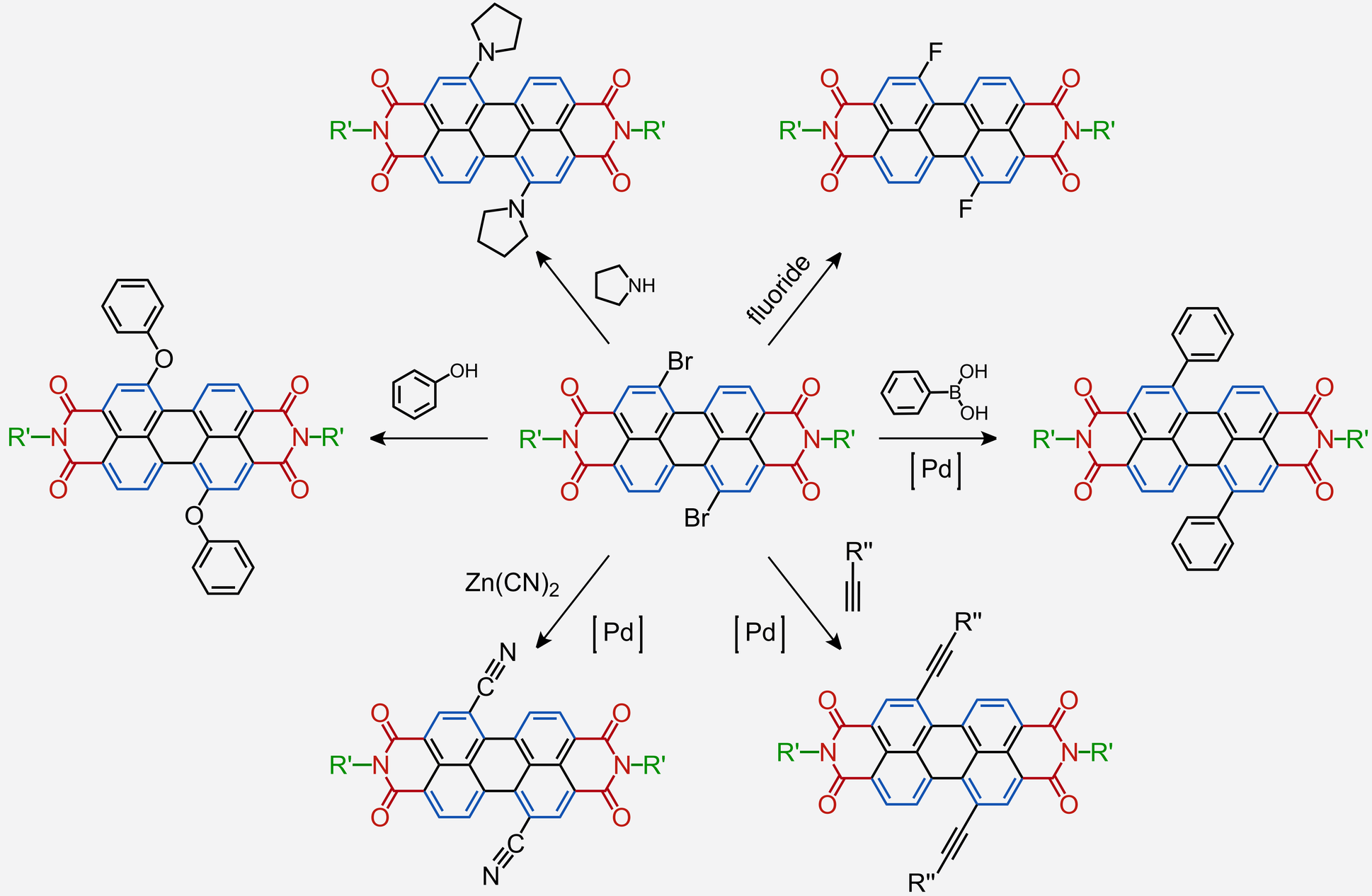
LUMO



HOMO

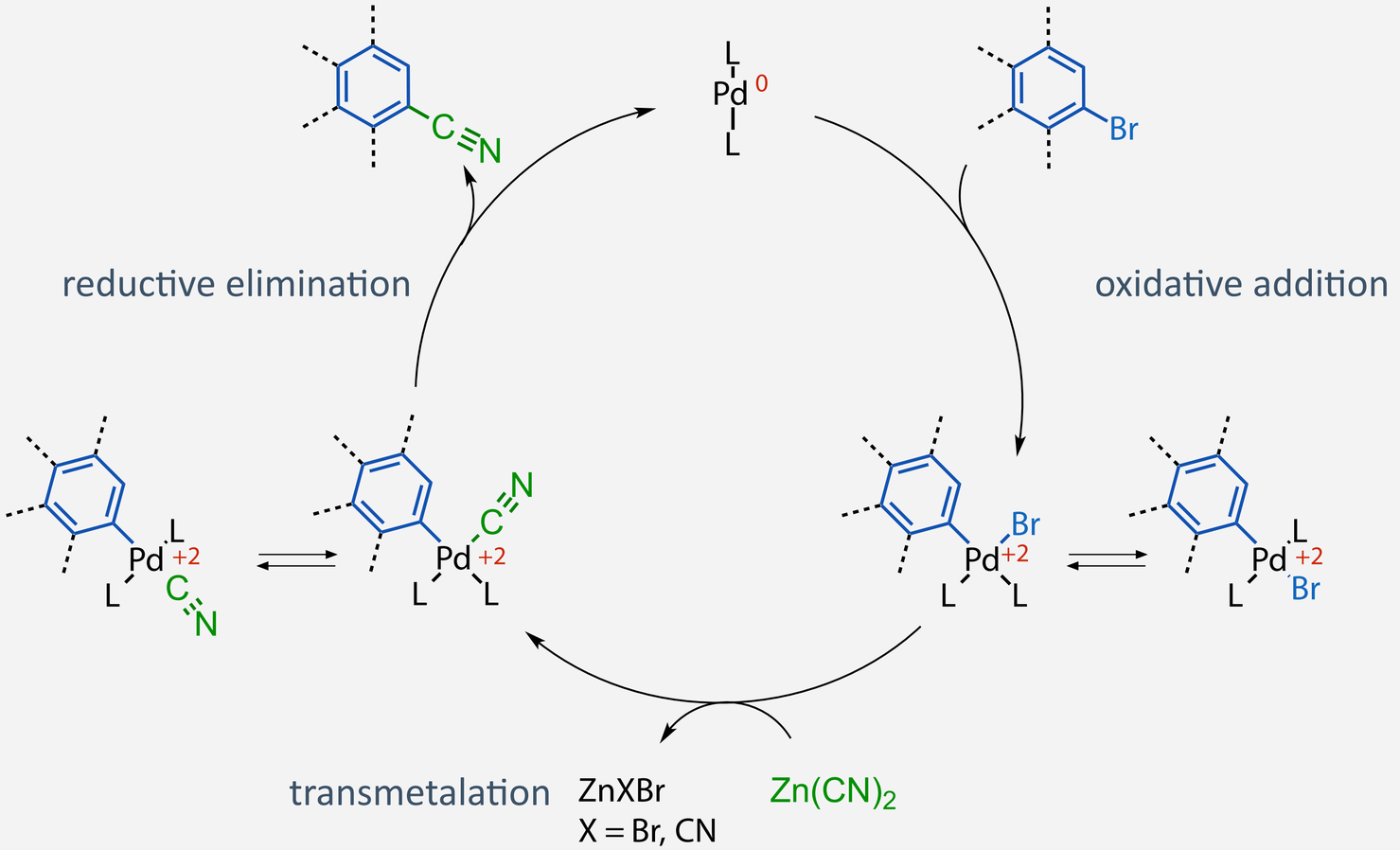
- **introduction of solubilizing groups by amide formation (little effect on electronic properties)**
- **substituents in bay position for tuning optical and electronic properties**

Bay Functionalization of Perylene Derivatives



M. R. Wasielewski, *Chem. Mater.* **2003**, 15, 2684

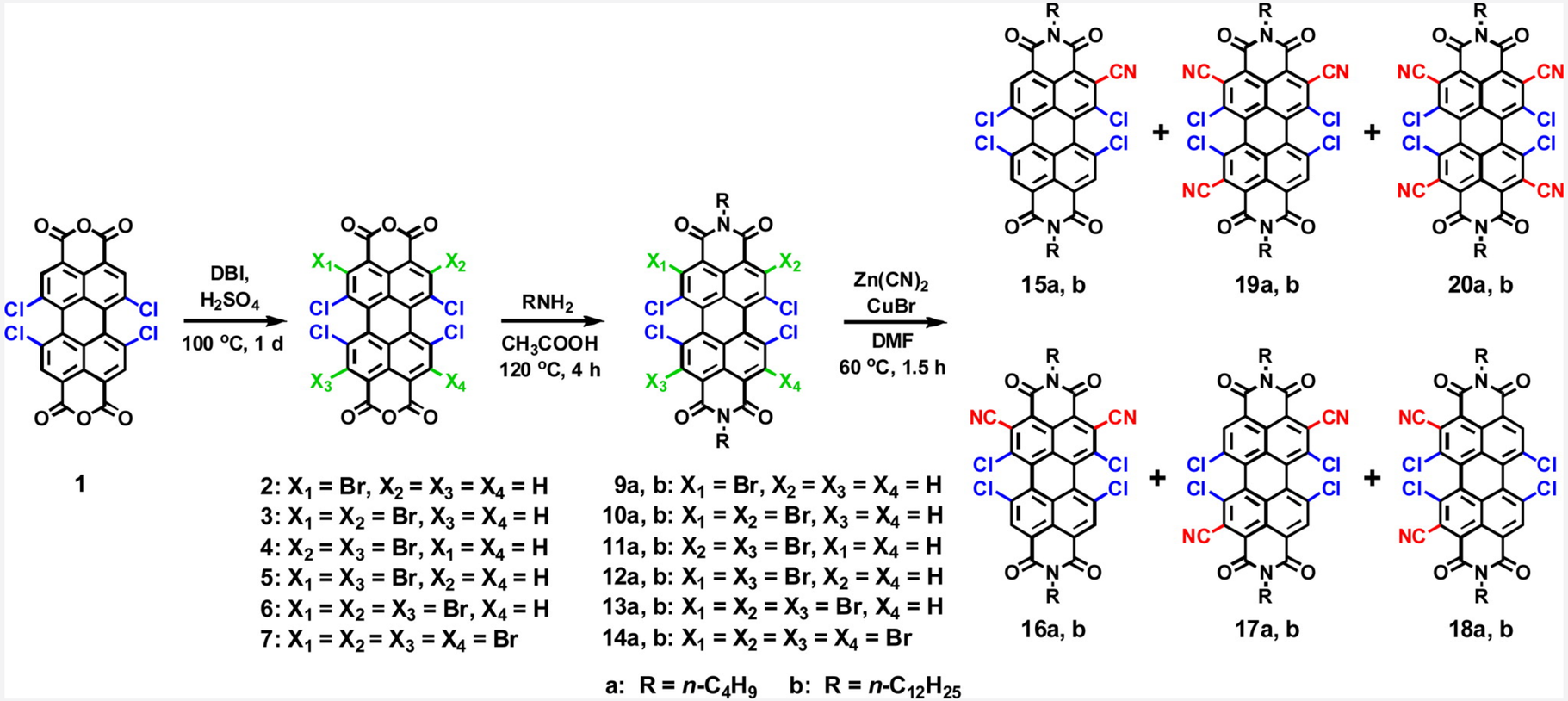
Proposed Mechanism of Perylene Diimide Cyanation



F. G. Buono, *Org. Lett.* **2008**, *10*, 5325

Band Gap Tuning of Perylene Bisimides

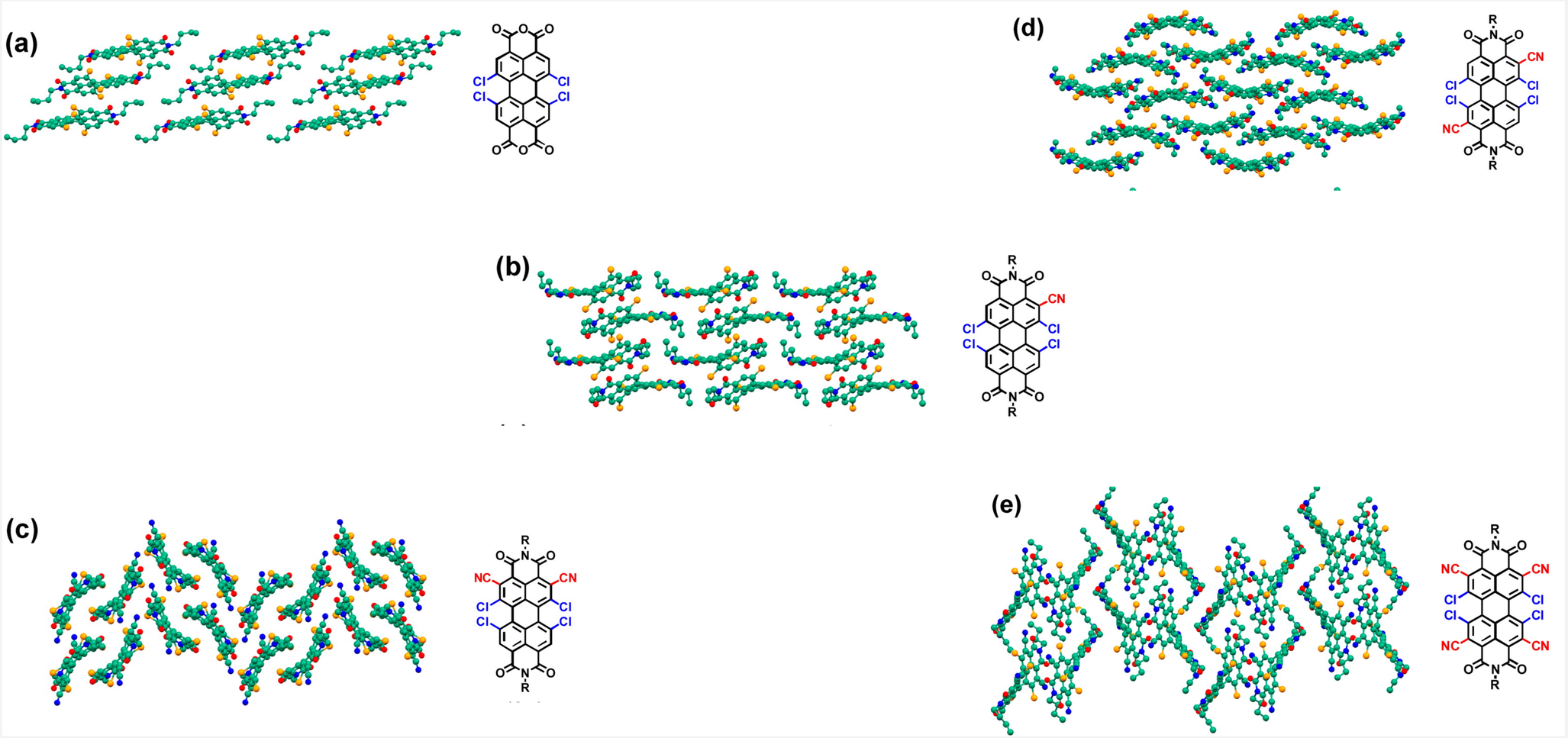
- reactions on non-bay positions to tune electronic properties
- CN substituted perylenes in a one pot-synthesis



- **instead oxidative or reductive homocoupling reactions or metal-catalyzed cross-couplings**

Band Gap Tuning of Perylene Bisimides

- substituents modify electronic density and molecular interactions for crystal packing

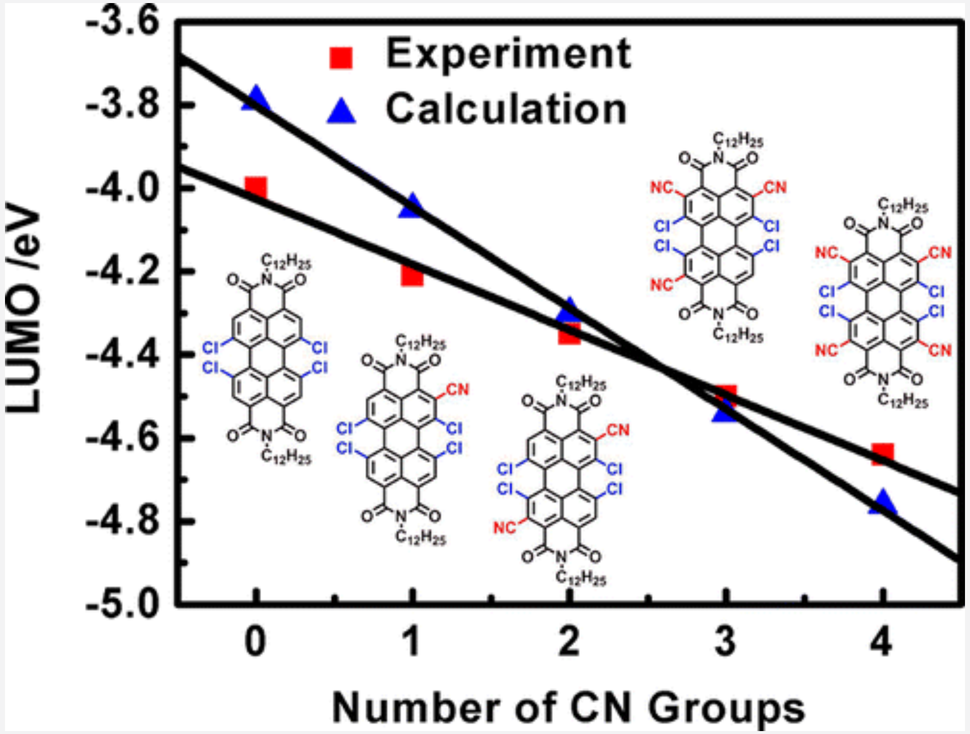


- **instead oxidative or reductive homocoupling reactions or metal-catalyzed cross-couplings**

Wang, *Organic Letters* **2014**, *16*, 394

Band Gap Tuning of Perylene Bisimides

- CN substituents successively decrease the LUMO level
- linear correlation with the number of substituents



- **observed LUMO energies correlate well with DFT calculations**