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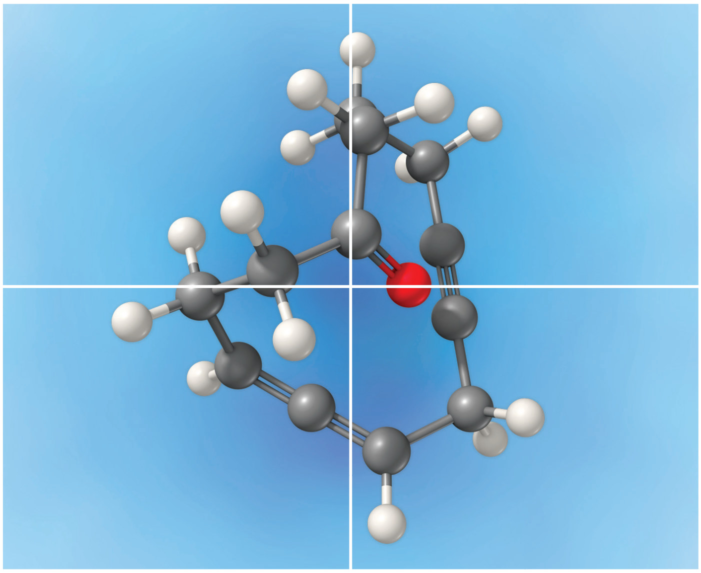

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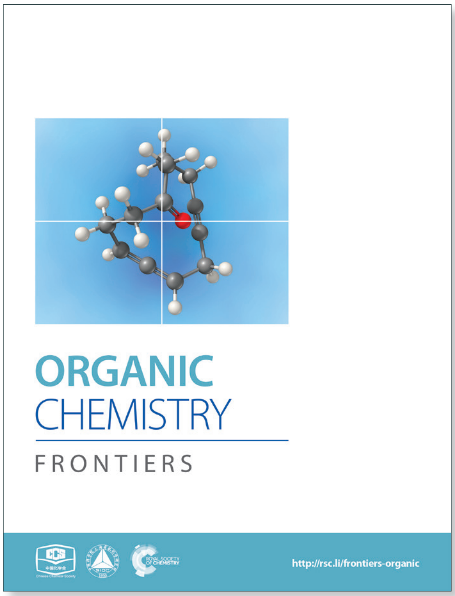

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Negishi coupling in the synthesis of advanced electronic, optical, electrochemical, and magnetic materials†

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†Dedicated to Professor Ei-ichi Negishi on the occasion of his 80th birthday.

Abstract

The Negishi coupling is one of the most important modern organic synthetic methods for the selective C–C bond formation, and has been extensively applied to the synthesis of organic electronic, optical, electrochemical, and magnetic materials. This report provides a critical overview of the efficiency and versatility of the Negishi coupling as applied to synthesizing polymers, oligomers, and small molecules with a wide variety of structural features and various desirable functions for organic electronic, optoelectronic, and other advanced technologies.

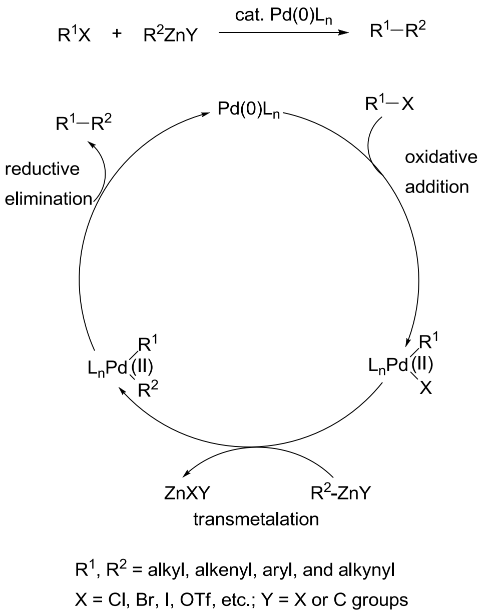
1. Introduction

The Negishi coupling may be loosely defined as the palladium or nickel catalyzed cross-coupling reactions of organometals containing metals of intermediate electronegativity represented by Zn, Al, and Zr with organic electrophiles such as organic halides and sulfonates.[1] Since its discovery in the middle to late 1970s,[2-7] the Negishi coupling has become a frequently used C–C bond formation method in modern organic synthesis.[8-19] For his pioneering work in the field of palladium-catalyzed cross coupling reactions and the impact of the Negishi coupling on organic synthesis, Professor Negishi, together with

Professors Heck and Suzuki, was awarded the 2010 Nobel Prize in chemistry.[19] The methodological developments of the Negishi coupling and its applications to the synthesis of organic molecules of chemical, biological, or medicinal importance have been extensively reviewed.[1, 9- 23] However, its utility in the synthesis of molecules of electronic, optical, electrochemical, or magnetic importance has not been reviewed. Organic materials with excellent electronic[24] and optical properties[25] are the key components in organic electronic and optoelectronic technologies such as organic light-emitting diodes (OLEDs), organic photovoltaic cells, and organic field-effect transistors (OFETs). Organic electronic and optoelectronic technologies offer several advantages over conventional technologies based on inorganic semiconductors, two of which being the low cost of production and the flexibility of the devices. Some of the organics-based technologies, for instance, OLED display technology, have been developed into a considerably advanced stage, and have resulted in the marketing of commercial products. The material development has made a major contribution to advancing these technologies. A number of reviews have dealt with applications of palladium-catalyzed cross coupling reactions (Kumada coupling,[26] Negishi coupling, Stille coupling,[27] and Suzuki coupling[28]) in the synthesis of polymeric and oligomeric electronic conducting and semiconducting materials.[29] Functional small molecules such as charge-transporting, redox-active, light-emitting and harvesting, and other optical materials have also played important roles in fabricating highly efficient organic electronic and optoelectronic devices. The Negishi coupling, particularly with the use of organozinc reagents, has enabled cross coupling of all types of carbon atoms, namely sp, sp^2, and sp^3 carbons, and essentially all possible combinations of various types of organozincs and electrophiles to form carbon-carbon bonds.[16] Therefore, the Negishi coupling becomes a frequent choice in synthesizing these small functional molecules as well. This review will focus on the application of the Negishi coupling in the synthesis of advanced materials including polymers, oligomers, and small functional molecules. The main objective of this review is to demonstrate the versatility and general applicability of the Negishi coupling in the synthesis of diverse arrays of functional molecules.

The generally accepted mechanism for the Negishi coupling with organozinc reagents is shown in **Scheme 1**. The reaction involves the oxidative addition of the organic electrophile, typically a halide or a sulfonate ester, to the palladium (0), the transmetalation with the organozinc reagent, and the reductive elimination to release the cross-coupling product and regenerate the catalyst. The Negishi coupling becomes the choice of methods mainly because of a few beneficial factors to organic synthesis which distinguish the Negishi coupling from other cross couplings using organometals of Sn (Stille coupling), B (Suzuki coupling), and Mg (Kumada coupling). First, the Negishi coupling proceeds with generally high efficiency, namely high yields and high selectivities. The selectivity could include the selectivity of the formation of the cross-coupled product and the stereoselectivity in the formation of structurally defined alkenes. Second, the Negishi coupling has optimal balance between reactivity and chemoselectivity. Organozinc reagents are more reactive than their Sn and B counterparts, and can tolerate more functional groups than Grignard reagents. Owing to the higher reactivity of organozinc reagents, the Negishi coupling can survive the presence of organic tin and boron functionalities, which permits the development of the sequential Negishi-Stille or Negishi-Suzuki coupling methodology and other useful synthetic strategies.[30] Third, the Negishi coupling often proceeds under mild conditions. Unlike the Suzuki and the Stille couplings, the cross coupling with organozinc reagents typically does not require a base or other additives. Another feature of the Negishi coupling is its operational simplicity. The organometals (Al, Zr, and Zn) used in the Negishi coupling can be generated in situ and used directly in the subsequent cross coupling. Last but not least, there are multiple convenient and inexpensive accesses to organozinc reagents including the transmetalation with organolithiums and

Grignard reagents, and particularly, the direct zinc insertion to organic halides.[30-35] Unlike the Stille coupling using toxic organostannes, the Negishi coupling with organozincs is environmentally benign.



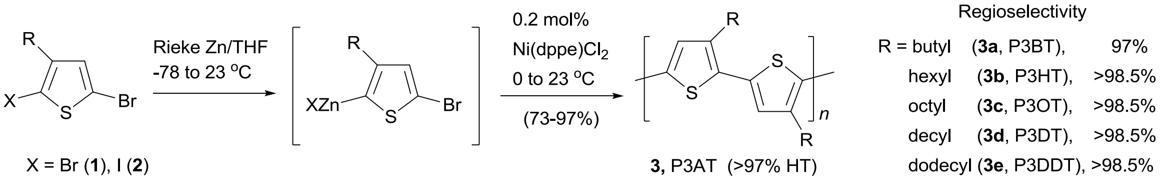
Scheme 1. Mechanism of the Negishi coupling with organozinc reagents.

2. Organic electronic materials

2.1. Conducting polymers via the Negishi polycondensation

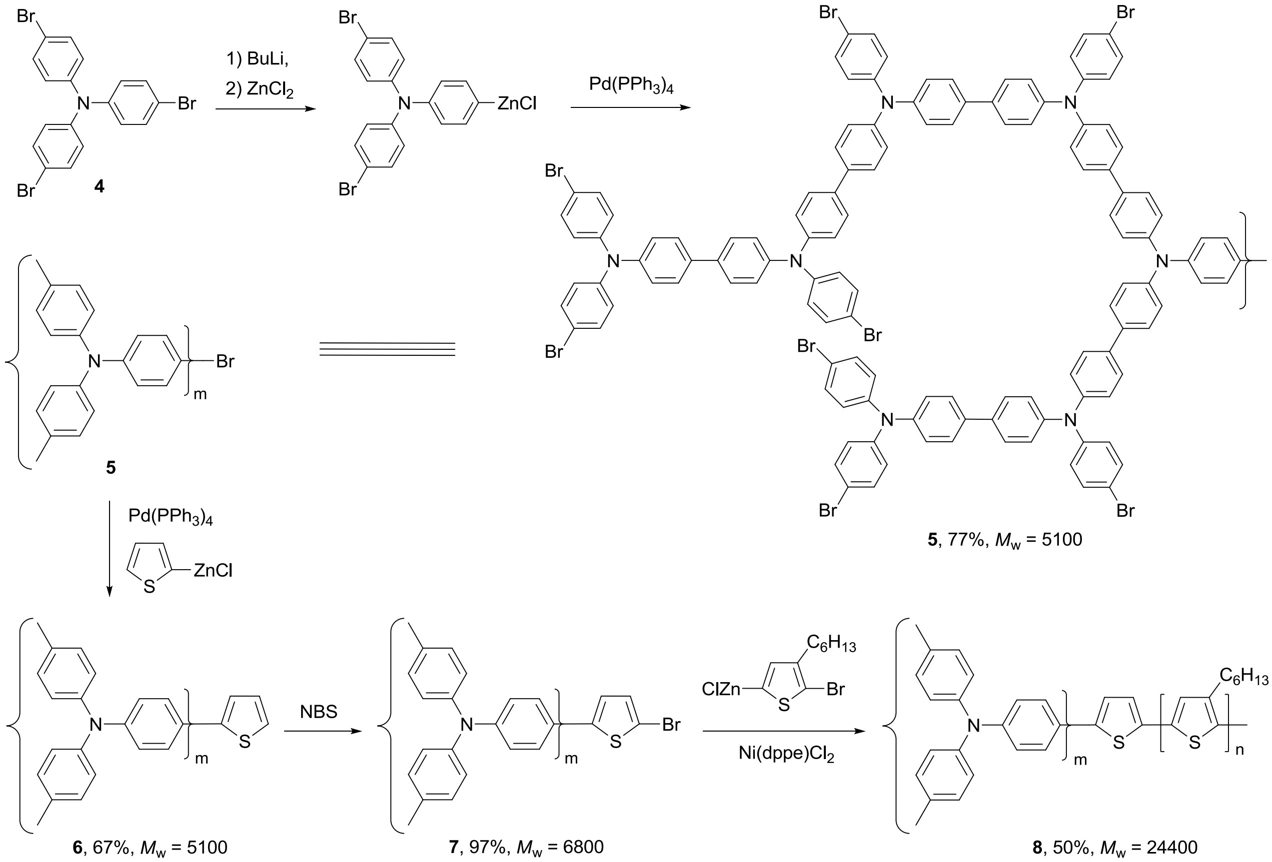
Polythiophenes are a family of conjugated polymers with excellent conductivity, and in particular, those derived from 3-alkyl-substituted thiophenes[36] have been used extensively in the polymer-based electronic devices including OLEDs,[37] OFETs,[38] and organic solar cells.[39] Regioselectivity (regioregularity) in the polymerization of 3-alkylthiophenes has profound influence on the conductivity of the formed polymers. Regioregular polymers usually display much higher conductivity than their regiorandom forms. Regioregular, head-to-tail poly(3-alkylthiophenes) (P3AT) can be prepared with excellent selectivity from the Ni-catalyzed cross coupling of the corresponding thiophenylzinc reagents.[40] The organozinc reagents can be generated by selective insertion of Rieke's zinc to either the

3-alkyl-2,5-dibromothiophene (**1**) at −78 ^{o}C or the 3-alkyl-2-bromo-5-iodothiophene (**2**) at 0 ^{o}C (**Scheme 2**). The polycondensation of these bifunctional organozinc reagents in the presence of catalyst $NiCl_2$(dppe) (dppe = 1,2-Bis(diphenylphosphino)ethane) produced polymers **3** in greater than 97% head-to-tail regioselectivity. Such polycondensation is termed AB-type polycondensation since the bifunctional monomer bears both metal and halide groups required for the cross coupling. The regioselectivity was found to depend on both the metal and the ligand of the catalyst. Replacement of dppe with PPh_3 or switch from Ni to Pd results in much lower selectivity. The regioregular polymers show consistently lower band gaps and thus higher conductivities (10^3 S/cm for doped films) compared to their regiorandom forms (<10 S/cm).[41]



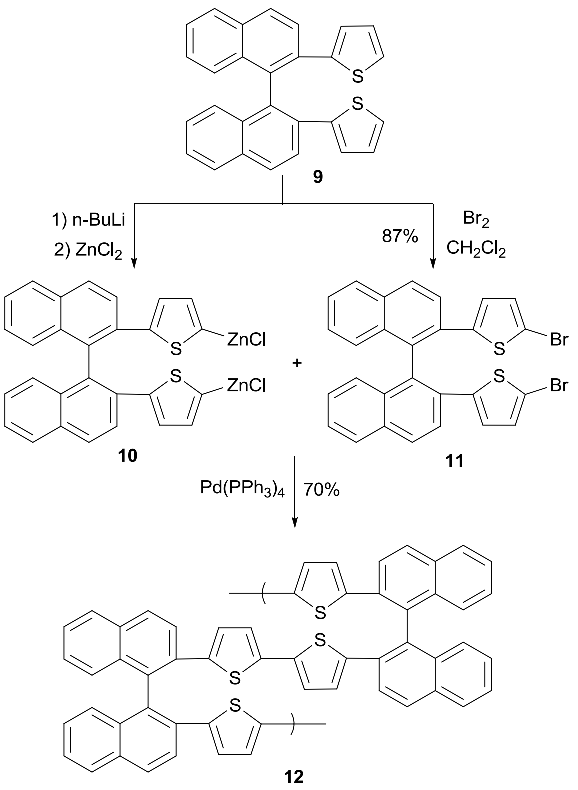
Scheme 2. Synthesis of P3ATs **3a**-**3e** by the Negishi polycondensation.

A star structured regioregular poly(3-hexylthiophene) with a conjugated hyperbranched poly(triphenylamine) was prepared by two consecutive Negishi polycondensations (**Scheme 3**)[42] First, a hyperbranched poly(triphenylamine) **5** was synthesized by a Negishi polycondensation starting from tris(4-bromophenyl)amine (**4**). The terminal bromo groups on the hyperbranched polymer **5** were subsequently converted to a thiophene by the Negishi coupling with 2-thioenylzinc chloride to form **6**, which was brominated with NBS to give **7**. This functionalized hyperbranched polymer **7** is used as a core for the synthesis of the star structured polymer **8**. The formation of regioregular P3HT was realized by the second Negishi polycondensation of 5-bromo-4-hexyl-2-thioneylzinc chloride. The star structured polymer has been shown to be electroactive and able to attain high level of conductivity up to 100 S/cm in its doped form.



Scheme 3. Synthesis of star structured polymer **8**.

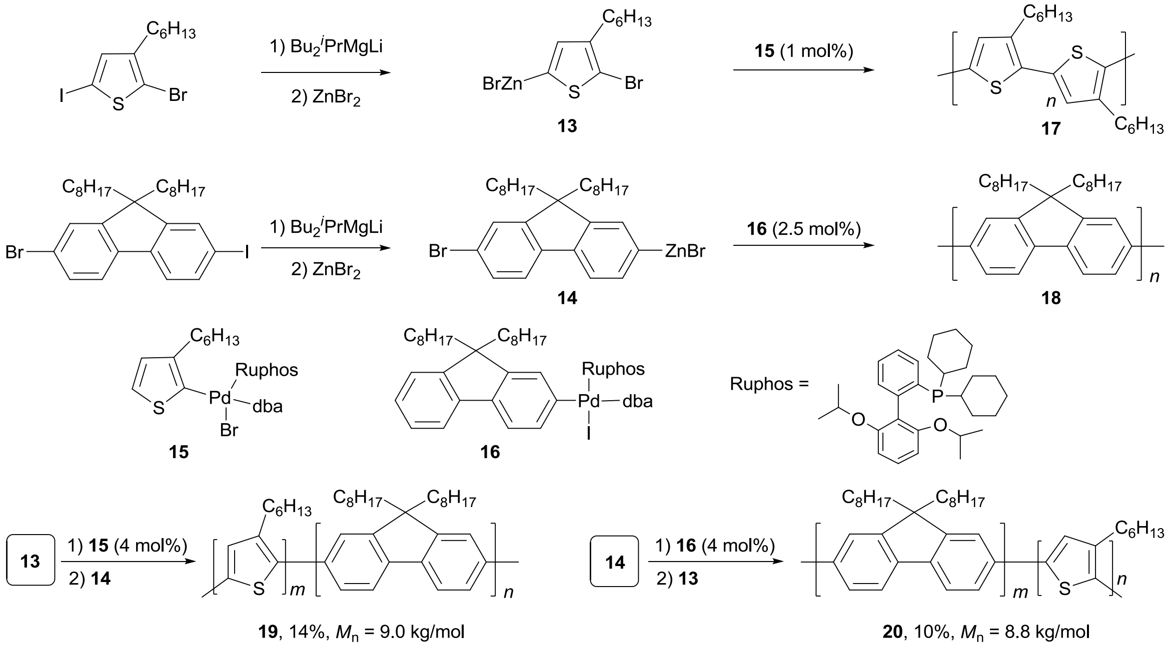
In a convergent synthesis shown in **Scheme 4**, 2,2’-Di(2-thiophenyl)-1,1’-binaphthylene (**9**) is converted to its bifunctional organozinc monomer **10** and dibromide monomer **11**, respectively. In the presence of Pd(PPh$_3$)$_4$, an AA/BB-type (two different bifunctional monomers AA and BB with each bearing two same functional groups) of polycondensation produces binaphthylene-thiophene copolymer **12** where the oligothiophene is covalently bonded to 2,2’-site of 1,1’-binaphthylene. The conductivity of the doped polymer was measured to be 3×10^{-5} S/cm.[43]



Scheme 4. Synthesis of Binaphthylene-thiophene copolymer **12**.

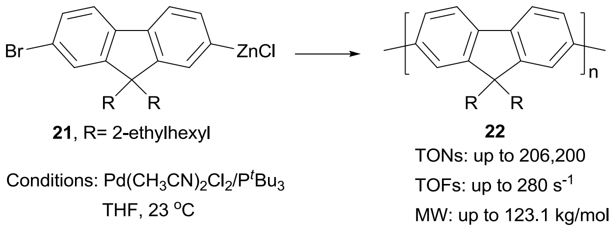
Polyfluorenes (PFs) represent another class of synthetic polymers that have required electronic and very favorable optical properties for applications in organic electronic and optoelectronic technologies.[44,45] Earlier synthesis of polyfluorenes was achieved with oxidative polymerization either chemically or electrochemically. A more controlled synthesis now relies on transition metal catalyzed cross coupling reactions. A universal chain-growth polymerization protocol was developed and demonstrated for the synthesis of both homopolymers, P3HT **17** and PF **18**, and block-copolymers P3HT-b-PF (**19**) and PF-b-P3HT (**20**) (**Scheme 5**).[46] The protocol is based on the Negishi coupling using a stable palladium catalyst with electron-rich, sterically hindered Ruphos[47] as the ligand. This method allows the one-pot synthesis of block-copolymers by successive monomer addition. The AB-type monomers **13** and **14** were generated by reacting 2-bromo-5-iodo-3-hexylthiophene and 2-bromo-7-

iodo-9,9-dihexylfluorene with ^{i}PrMgCl-LiCl,[48] followed by the treatment with $ZnBr_2$. The initiators **15** and **16** were prepared by oxidative addition of 2-bromo-3-hexylthiophene and 2-iodo-9,9-dioctylfluorene to $Pd_2(dba)_3$ (dba = dibenzylideneacetone) in the presence of Ruphos.



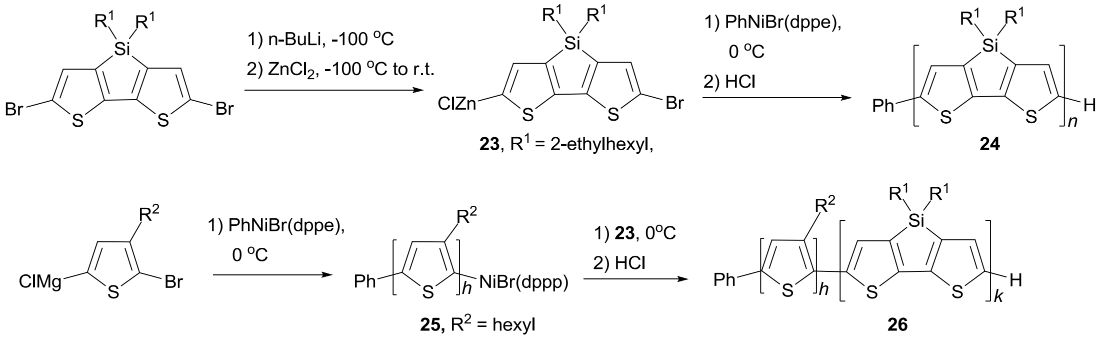
Scheme 5. Synthesis of P3HT(**17**), PF(**18**), P3HT-b-PF(**19**), and PF-b-P3HT(**20**).

Although the π-conjugated polymers are often synthesized by the Stille[29c] and the Suzuki[29a] polycondensations, a recent study demonstrates that the Negishi polycondensation can offer several critical advantages such as higher reactivity, lower catalyst loading, and higher molecular weight (MW).[49] Kiriy and co-workers reported the Pd/$P^{t}Bu_3$-catalyzed Negishi chain-growth polycondensation of AB-type monomer **21** to produce the polyfluorene **22**, which proceeds with unprecedentedly high turnover numbers (TONs) of over 100,000 (highest TONs of 206,200) and turnover frequencies (TOFs) of up to 280 s^{-1}. The highest MW of 123.1 kg/mol was obtained at the monomer/catalyst ratio of 20,000:1(**Scheme 6**). They also demonstrated that the related AA/BB-type step-growth polycondensation proceeds with two orders of magnitude lower TONs and TOFs under the same conditions.



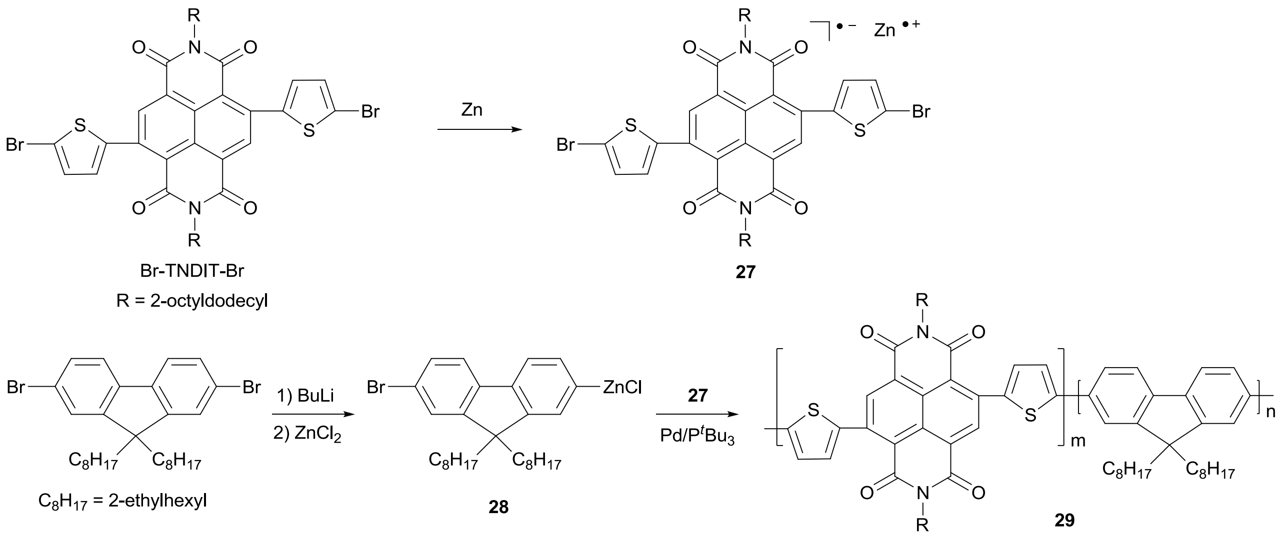
Scheme 6. Highly efficient synthesis of polyfluorene by the Negishi polycondensation.

A quasi-living Negishi-type catalyst-transfer polycondensation of a zinc–organic DTS-based monomer **23** provides an access to narrowly distributed poly(4,4-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]silole (PDTS) (**24**) with controlled molecular weight (**Scheme 7**).[50] The synthesis of well-defined all-conjugated diblock copolymers **26** containing a PDTS block is accomplished by a combination of Kumada and Negishi catalyst-transfer polycondensations (KCTP and NCTP, respectively). Notably, it was shown that living P3HT chains **25** obtained by KCTP of magnesium–organic thiophene-based monomer efficiently initiate NCTP of zinc–organic DTS-based monomer **23**. The purity of the DTS-based monomer was found to be a crucial factor for achieving a clean chain-growth polymerization process.



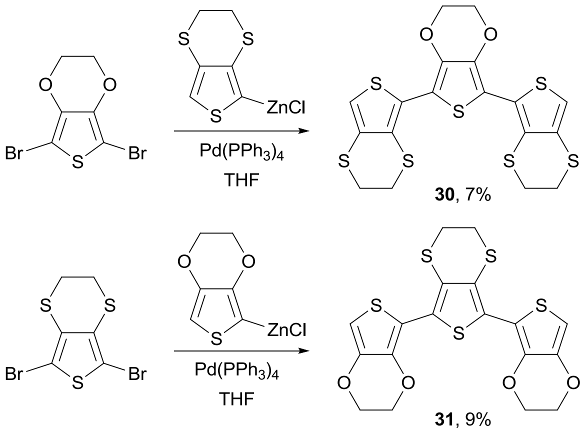
Scheme 7. Synthesis of diblock copolymer **26** using a combined KCTP and NCTP

The chain-growth catalyst-transfer Negishi polycondensation has recently been successfully applied to the copolymerization of electron-rich and electron-deficient monomers,[51] anion-radical **27** formed upon reaction of activated Zn powder and Br−TNDIT−Br (Br−TNDIT−Br = 2,6-bis(2-bromothien-5-yl)naphthalene-1,4,5,8-tetracarboxylic- N,N′-bis(2-octyldodecyl) diimide) and AB-type fluorine-based monomer **28** generated from monolithiation of 2,7- dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene followed by transmetalation with $ZnCl_2$. The copolymerization proceeds rapidly in the presence of Pd catalyst having bulky and electron-rich tri-tert-butylphosphine ligand. Even though the two monomers are simultaneously added, the polymerization gives sharp gradient copolymer or even block-like copolymer **29**, which is owing to much faster Negishi condensation of the fluorenic monomer **28**.[49]



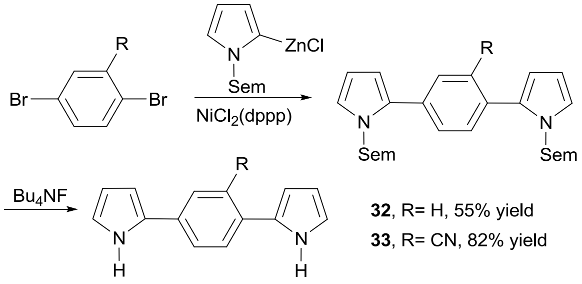
Scheme 8. Synthesis of block copolymer **29**.

The Negishi coupling is also frequently used to synthesize monomers for other polymerization reactions. Poly(ethylene-3,4-dioxythiophene) (PEDOT) has become one of the most popular polythiophene derivatives used for device applications, due to its exceptional hole injection properties, high conductivity and stability.[52,53] PEDOT-PSS (PEDOT-polystyrene sulfonic acid) is now a standard hole injection material used in solution-processed OLED devices and solar cells. The p-doped PEDOTs have demonstrated conductivity of several hundred S/cm, whereas the sulfur analog of PEDOT, poly(ethylene-3,4-dithiathiophene) (PEDTT) showed electrical conductivity of 0.1 and 0.4 S/cm in its chemically doped (with $FeCl_4^-$) and electrochemically doped (with ClO_4^-) states, respectively.[54]The large difference in band gap between PEDOT and PEDTT promoted Skabara and co-workers to synthesize a hybrid copolymers PSOS and POSO and compare their electronic and electrochemical properties.[55] The monomers SOS (**30**) and OSO (**31**) were synthesized as shown in **Scheme 9**.



Scheme 9. Synthesis of monomers SOS (**30**) and OSO (**31**).

Dipyrrolylphenylenes **32** and **33** were prepared by the nickel-catalyzed cross coupling of *N*-Sem-pyrrol-2-ylzinc chloride (Sem = [2-(Trimethylsilyl)ethoxy]methyl) and the appropriate dibromo derivatives (**Scheme 10**).[56] The Sem protecting group can be easily removed by reacting with Bu_4NF (TBAF). Anodic coupling of monomers **32** and **33** produced conducting conjugated polymers poly-**32** (σ = 0.3 S/cm) and poly-**33** (σ = 0.1 S/cm), respectively.

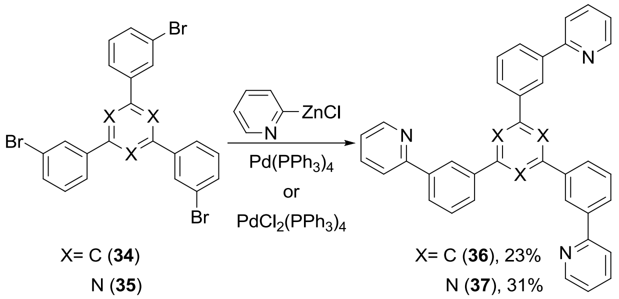


Scheme 10. Synthesis of dipyrrolylphenylenes **32** and **33**.

2.2 Small molecule semiconducting materials

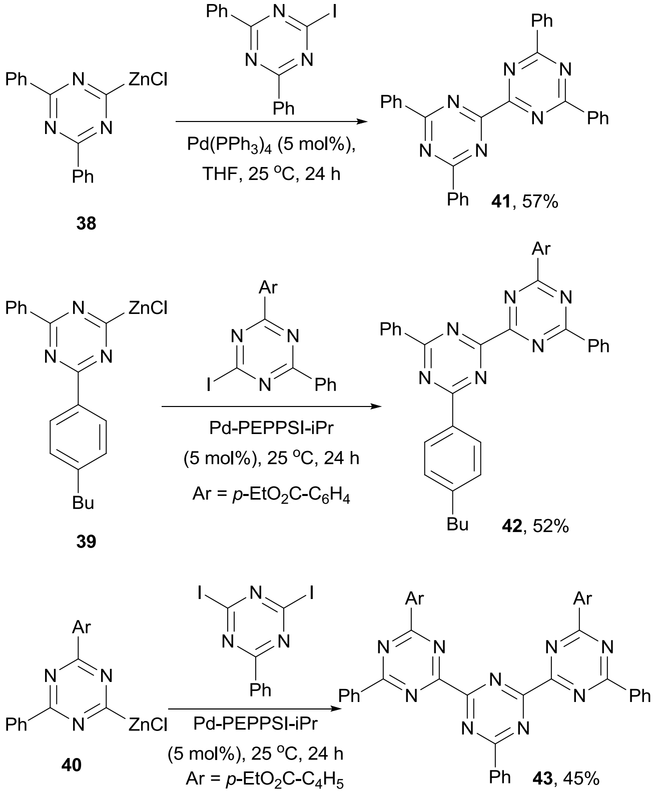
Since the discovery of vapor-deposited OLED[57] and photovoltaic[58] devices with a p-n junction structure, small molecules have attracted a great deal of attention in order to improve the efficiency and stability of the devices. In general, these small molecules can be divided into electron-transporting and hole-transporting materials. Electron transporting materials should have a relatively low-lying LUMO, and typically contain electron-deficient heteroaromatic structures, while the hole-transporting materials are dominated by the triarylamines that can form a stable radical cation. A material capable of transporting/trapping both electrons and holes may be used as the host in the emissive layer of an OLED device to enhance the device performance.[59]

Electron transporting materials. 1,3,5-Tri(m-pyrid-2-yl-phenyl)benzene (**36**) was synthesized by using Negishi coupling of 1,3,5-tri(m-bromophenyl)-benzene (**34**) with 2-pyridylzinc bromide[60] and evaluated as electron transporting materials in OLED devices (**Scheme 11**), which was compared with isomeric 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene and 1,3,5-tri(m-pyrid-4-yl-phenyl)benzene prepared by the Suzuki coupling. Similar Negishi coupling was applied to the syntheis of 1,3,5-triazine-core-containing eletrontransporting material **37**.[61]



Scheme 11. Synthesis of **36** and **37**.

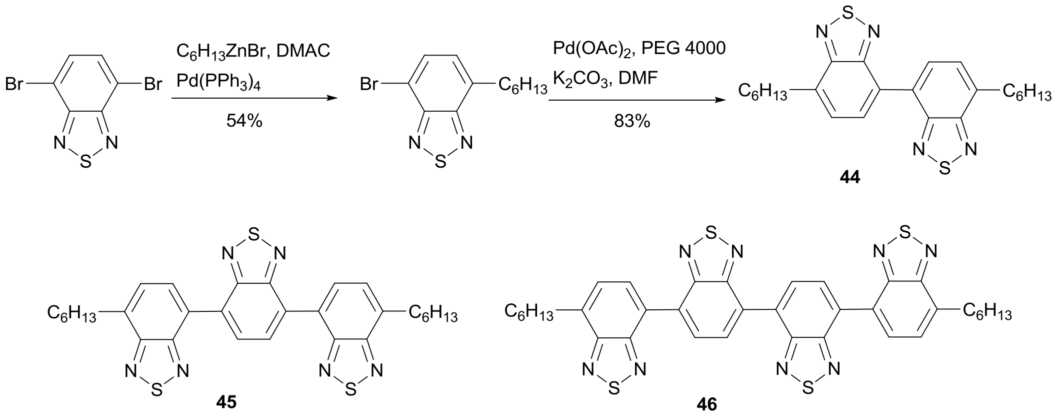
Knochel and co-workers developed a method of generating 2-zincated 1,3,5-triazines via an iodine-magnesium exchange of iodo- and diiodo-1,3,5-triazines with alkyl Grignard reagents followed by tansmetalation with $ZnCl_2$.[62] The zinc reagents **38-40** undergo palladium catalyzed cross coupling with iodo- or diiodo-1,3,5-triazines to give dimeric and trimeric derivatives **41-43**, respectively, in moderate yields (**Scheme 12**).[62] These materials could be used as electron-transporting materials in optoelectronic devices.[63]



Scheme 12. Synthesis of oligomeric 1,3,5-triazines **41-43**.

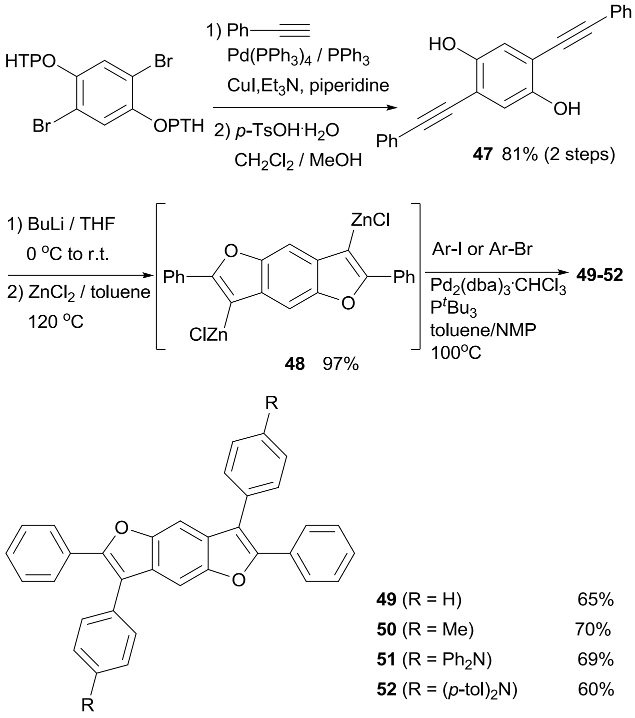
Electron-deficient 2,1,3-benzothiadiazole oligomeric assemblies **44-46** were prepared through palladium-mediated homo-coupling or cross coupling (**Scheme 13**).[64] To improve the solubility of the oligomers, an alkyl group is introduced by the Negishi coupling using the alkylzinc reagent conveniently generated using Huo's protocol.[33] Compared with a commercial electron-transporting material 2-(4-

biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, compounds **45** and **46** show much lower LUMO values, suggesting that the energy barriers between the oligomers and the cathode would be greatly reduced when they are used in OLEDs. These optoelectronic properties show that the oligomers are promising electron-transporting materials. The introduction of an alkyl group improves the solubility of the material not only for easy isolation and purification but also for fabricating devices using low-cost solution-processes.



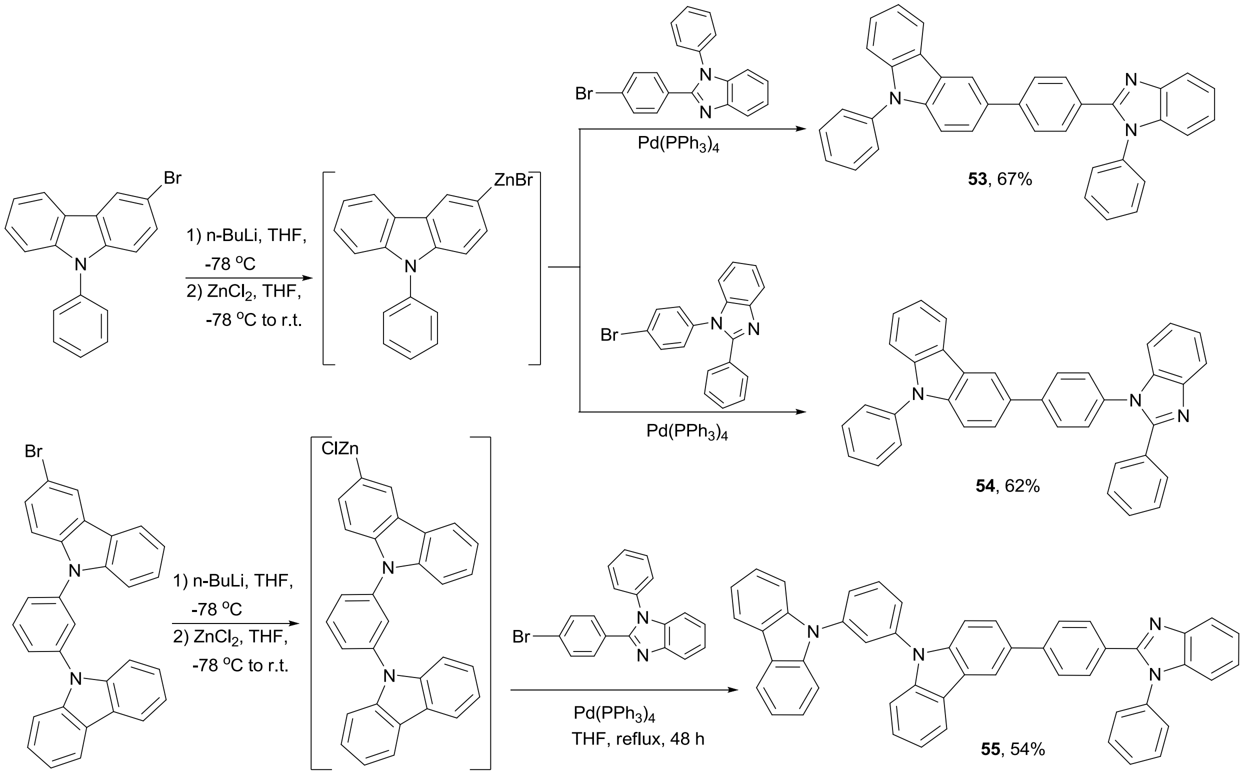
Scheme 13. Synthesis of alkylated oligomeric 2,1,3-benzothiadiazoles **44-46**.

Hole transporting materials. A series of 2,3,6,7-tetraarylbenzo-[1,2-*b*:4,5-*b*']difurans (BDFs) were synthesized based on a zinc-mediated annulation-Negishi coupling synthetic methodology.[65] The precursor **47** for the annulation was prepared by the Sonogashira coupling[66] of protected 2,5-dibromohydroqinone with phenylacetylene. Zinc-mediated annulation produced the 3,7-dizinciobenzodifuran **48** in quantitative yield, which underwent the Negishi coupling with arylzinc halides to give 2,3,6,7-tetraarylbenzo-[1,2-*b*:4,5-*b*']difurans **49-52** in good yields[65a] (**Scheme 14**). A toluene/*N*-methylpyrrolidinone (NMP) mixture was used as the solvent to improve the yields.[67] These compounds were evaluated as efficient hole transporting materials in OLED devices showing the performance comparable to or better than that of the device made with the commonly used hole transporting materials α-NPD (*N,N′*-Di(1-naphthyl)-*N,N′*-diphenyl-(1,1′-biphenyl)-4,4′-diamine).[68] Compounds **49**, **51**, and **52** have higher hole mobility ($\mu = 5.6 \times 10^{-4}$ to 2.8×10^{-3} cm^2/Vs) than α-NPD (($\mu = 3.6 \times 10^{-4}$ cm^2/Vs).[65a]



Scheme 14. Synthesis of **49-52** by the zinc-mediated annulation-Negishi coupling tandem process.

Bipolar host materials. Host materials are referred to the host used in the emissive layer of OLED devices. Bipolar hosts are able to transport both electrons and holes and have been used to improve performance of OLED devices,[59] in particular, to reduce the drive voltage and increase the efficiency. A series of hybrid bipolar host materials **53-55** were synthesized by linking a carbozole motif and a benzimidazole motif using the Negishi coupling method (**Scheme 15**).[69] These materials were successfully incorporated into the phosphorescent green and blue OLEDs as the host materials showing high external quantum efficiency. A carbazolyl-substituted BDF derivative, 2,6-diphenyl-3,7-bis[4-(N-carbazolyl)phenyl]benzo[1,2-b:4,5-b’]difuran, which was synthesized by using the same method shown in **Scheme 14**, also displays bipolar property and has been used to fabricate efficient OLED devices with a simple homojunction structure.[65c]



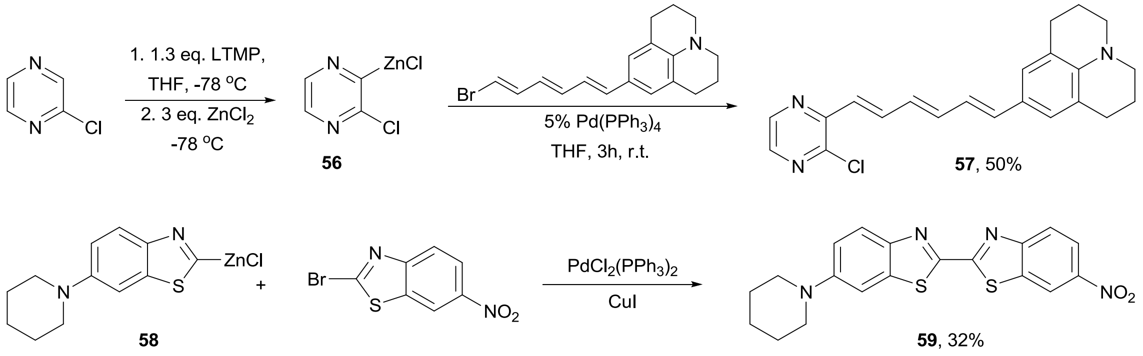
Scheme 15. Synthesis of hybrid bipolar host materials **53-55**.

3. Organic optical materials

Organic optical/photonic materials are referred as the molecules that can either interact with light, such as absorbing, reflecting, refracting, and rotating light, or emit light under stimulations. Organic optical materials that are important to organic electronic and optoelectronic devices include but are not limited to nonlinear optical (NLO) materials, liquid crystals, light emitters, and light harvesting materials. Transparency, namely lack of absorbing the visible light, is also an important optical property of organic electronic materials that can be an important component in the optoelectronic devices such as capsulation.

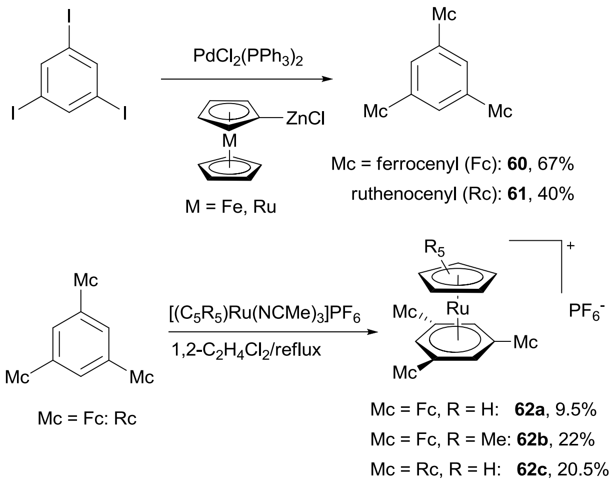
3.1 Nonlinear optical materials

A push-pull structure with a pyrazine core and hexatriene chain **57** was efficiently constructed by the reaction of the pyrazinyl zinc reagent **56** with 6-julolidinyl-1-bromohextriene in the presence of $Pd(PPh_3)_4$ (**Scheme 16**).[70] The organozinc reagent was generated in situ by deprotonating 2-chloropyrazine with LTMP (lithium 2,2,6,6-tetramethylpiperidide) followed by treating with zinc chloride. The molecule displayed promising NLO properties with a dipole moment of $\mu = 8.0$ D and the scalar product $\mu\beta$ of 1040×10^{-48} esu as compared to the DANS[71] (dimethylaminonitrostilbene) ($\mu = 6.6$ D; $\mu\beta = 350 \times 10^{-48}$ esu). In addition, the compounds also emitted intensely red light (653 nm) with a large Stokes shift (5783 cm^{-1}). Similar strategy was also applied to functionalizing 2,6-dichloropyrazine.[70] Another push-pull molecule 6-nitro-6'-piperidyl-2,2'-bisbenzothiazole (**59)** was prepared by palladium-catalyzed cross coupling of the organozinc derivative **58** and 2-bromo-6-nitrobenzothiazole (**Scheme 16**).[72] The zinc reagent was prepared by the deprotonation of 6-(N-piperidyl)benzothiazole with n-butyllithium at –100 °C followed by treating with zinc chloride. Compound **59** exhibited good NLO properties ($\mu\beta = 375 \times 10^{-48}$ esu) and a dual, oxidative and reductive, three-stage single-electron redox character.



Scheme 16. Synthesis of push-pull NLO materials **57** and **59**.

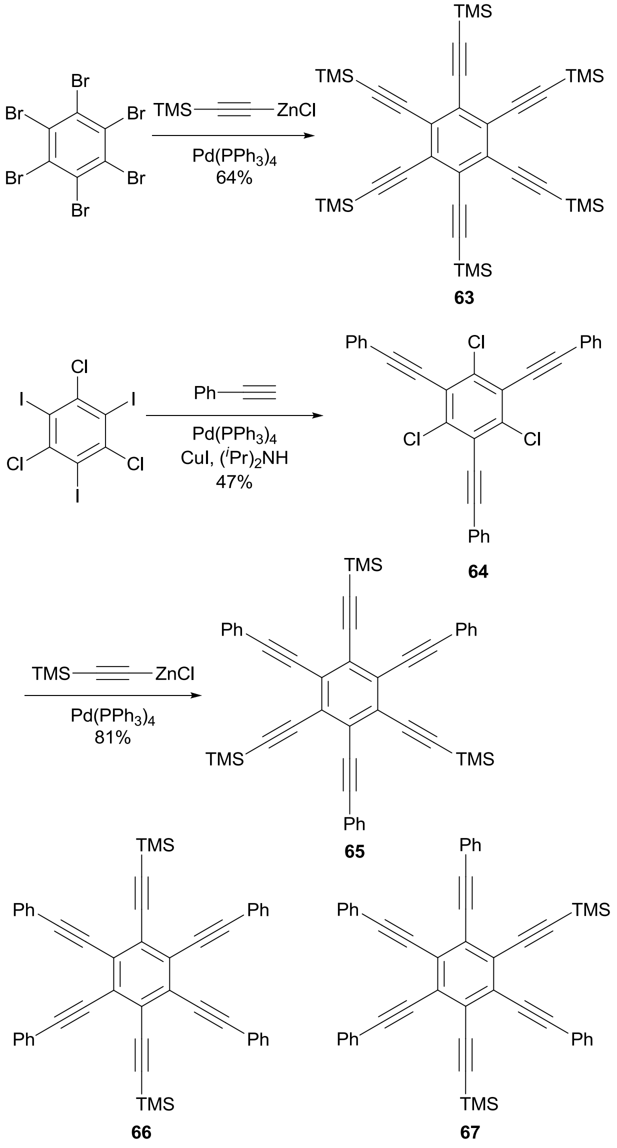
The Negishi cross-coupling reaction of 1,3,5-triiodobenzene with ferrocenyl- and ruthenocenylzinc chlorides yields the corresponding 1,3,5-trimetallocenylated benzene derivatives **60** and **61** in good yields (**Scheme 17**).[73] When 1,3,5-tribromobenzene was used, the yields were much lower, being 35% and 13% for **60** and **61**, respectively. The metallocenylzinc reagents were prepared by deprotonating the metallocenes with butyl lithium followed by treating with zinc chloride.[74] The resulting **60** and **61** were used as the ligands to synthesize the trigonal-pyramidal four-sandwich NLO materials **62a-c**. Compound **62a** demonstrates a larger first hyperpolarizability than the all-ruthenium congener **62c** due to the better electron-donating properties of the ferrocene substituents.



Scheme 17. Synthesis of the trigonal-pyromidal four-sandwich NLOphores **62a-c**.

3.2 Liquid crystals

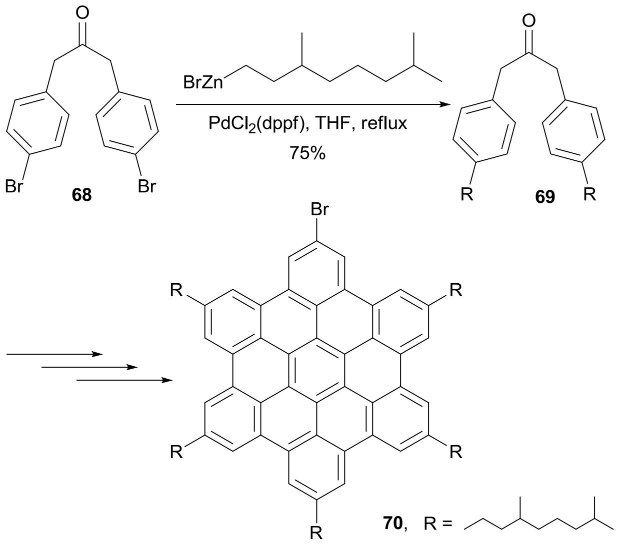
Hexaethynylbenzene derivatives are attractive molecules because of their potential applications as liquid crystals, nonlinear optical materials, core structures for dendritic materials, and building blocks for two-dimensional carbon network graphynes. Tobe and co-workers reported an efficient synthesis of hexaethynylbenzene **63**[75] (**Scheme 18**) using the Negishi alkynylation of hexabromobenzene. Toluene was added as the co-solvent to raise the refluxing temperature. The yields of **63** were much better than those reported previously using the Sonogashira coupling.[76, 77] On the other hand, the reaction of 2,4,6-trichloro-1,3,5-triazine with [(trimethylsilyl)ethynylzinc chloride in the presence of Pd(PPh$_3$)$_4$ catalyst proceeded smoothly at room temperature to give 2,4,6-tris[(trimethylsilyl)ethynyl]triazine in 80% yield, reflecting the higher reactivity of electron-deficient heteroaryl halides.[75] A stepwise Sonogashira and Negishi coupling reaction of chloroiodobenzene derivatives with appropriate ethynyl reagents efficiently produced differentially substituted hexaethynylbenzenes. For instance, the Sonogashira coupling of 1,3,5-trichloro-2,4,6-triiodobenzene with phenylacetylene produced **64** in 47% yield, which was further cross coupled with [(trimethylsilyl)ethynyl]zinc chloride in the presence of Pd(PPh$_3$)$_4$ to introduce three more ethynyl groups and give the hexasubstituted benzene **65** in 81% yield (**Scheme 18**).[75] The other two compounds **66** and **67** were prepared similarly from appropriate hexahalobenzenes. The Negishi coupling gives generally satisfactory yields. The success of this differential substitution method clearly benefits from the higher reactivity of organozinc reagents.



Scheme 18. Synthesis of hexaalkynylbenzenes **63** and **65**.

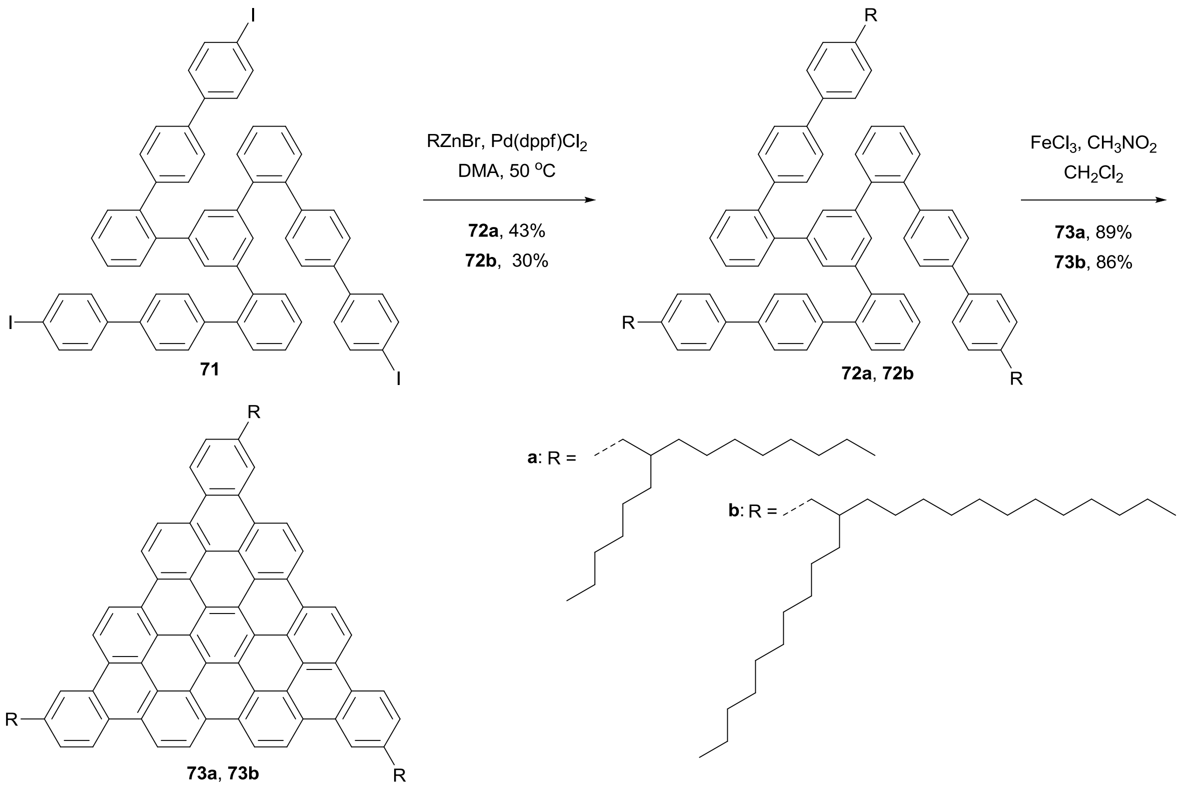
Alkyl- or phenyl-alkyl substituted hexabenzocoronenes (HBCs) are discotic liquid crystalline materials with extremely large phase widths (up to 250 °C)[78] and charge carrier mobilities along the columnar axis (1.13 cm^2/Vs).[79] In the synthesis of thermotropic liquid crystalline derivatives of hexabenzocoronene (HBC) substituted at the periphery by one bromo and five alkyl groups, palladium catalyzed cross coupling reactions were used to improve the synthesis of the HBC precursors.[80]

Specifically, the Negishi coupling was used to introduce the flexible alkyl chain in the synthesis of a precursor **69** that is used in the synthesis of the mono bromo HBC **70** (**Scheme 19**). The cross coupling of the dibromide **68** with 3,7-dimethyloctanylzinc bromide in the presence of $PdCl_2$(dppf) afforded **69** in 75% yield. The Kumada coupling with the Grignard reagent was also successful, but involves steps of tedious protecting and deprotecting the carbonyl group. It should be noted that in the absence of functional groups, the Kumuda coupling works very well as reported in this paper.



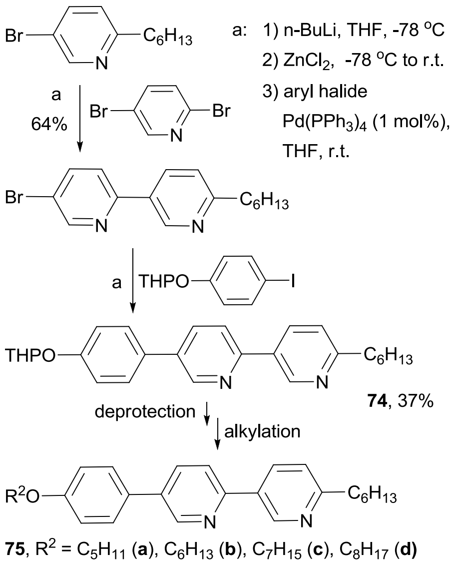
Scheme 19. Synthesis of alkylated hexabenzocoronene **70**.

In a synthesis of triangle-shaped discotic graphenes with three swallow-tailed alkyl substituents **73a** and **73b**,[81] a three-fold cross coupling is required to introduce the alkyl substituents. The Kumada coupling was unsuccessful because of inactivity and server homo-coupling of the magnesium reagents. The author then turned to the Negishi coupling using the corresponding zinc reagents easily prepared using Huo's protocol,[33] and the desired products **72a** and **72b** were obtained in reasonable yields (**Scheme 20**). Both **73a** and **73b** exhibit a characteristic discotic liquid crystalline phase with extremely high stability; they did not have an isotropic phase up to 500 ^{o}C. The introduction of the swallow-tailed substituents allows a facile purification, control over the thermotropic properties, and solution fabrication of highly efficient photovoltaic devices. When **73b** was blended with N,N'-bis(1-ethylpropyl)- 3,4,9,10-perylenetetracarboxy-diimide (PDI) in a ratio of 4:6, and was spin-coated to a photovoltaic device with the structure of indium tin oxide (ITO)/(**73b** + PDI)/Ag, an external quantum efficiency (EQE) of 19% at 490 nm of illumination was achieved.[81]



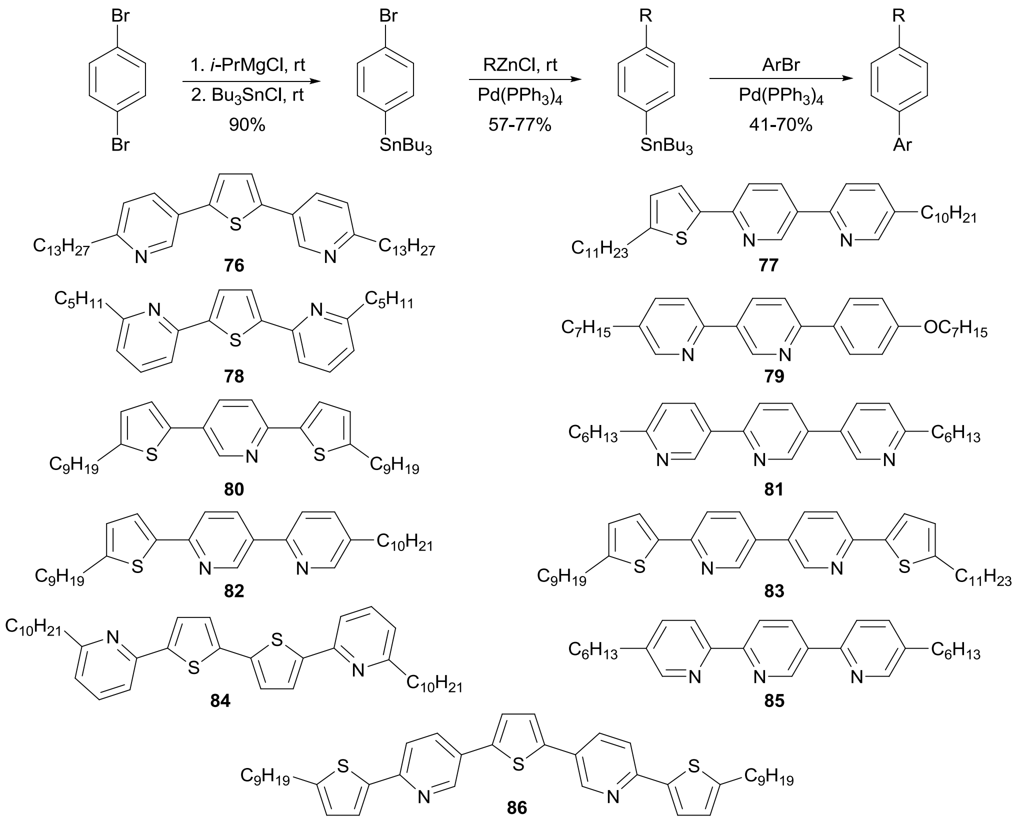
Scheme 20. Synthesis of alkylated triangle-shaped graphenes **73a** and **73b**.

Fifteen 2,5-disubstituted pyridine-based liquid crystals are synthesized by exploiting the different reactivity of the bromine atoms in 2,5-dibromopyridine under Negishi coupling conditions.[82] The use of consecutive Negishi couplings to prepare the precursor **74** is illustrated in **Scheme 21**.



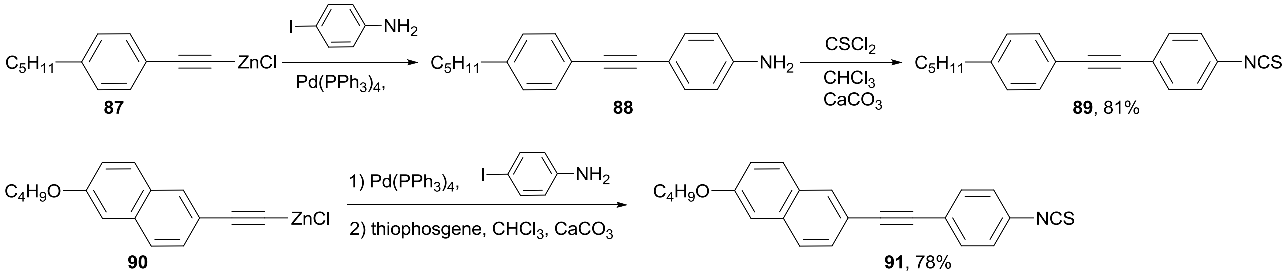
Scheme 21. Syntheis of liquid crystals **75a-d**.

The high reactivity of organozinc reagents in the Negishi coupling has been often exploited in the selective cross coupling in the presence of less reactive stannyl and boron groups. For example, the 2-bromo-5(or 6)-tributylstannylpyridines, prepared from the dibromopyridines and *i*-PrMgCl at room temperature, undergo Negishi coupling with either alkyl or arylzinc chlorides without affecting the tributylstannyl group (**Scheme 22**).[83] The newly produced alkyl- and arylsubstituted pyridylstannanes are suitable for further functionalization by the Stille coupling, which resulted in the synthesis of a group of 11 liquid crystalline materials **76-86** with aromatic cores comprised of pyridine and thiophene rings.



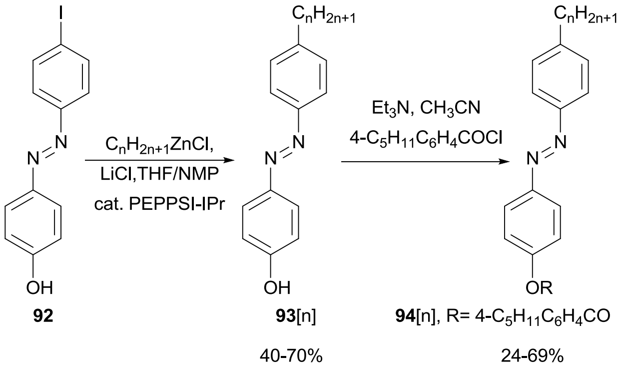
Scheme 22. Negishi coupling in the presence of the organostanyl functional group.

A number of structural moieties including core units (such as phenyl, naphthyl and thiophenyl), linking groups (such as ethynyl), terminal substituents (such as cyano, isothiocyanato and fluoro), and lateral fluoro substituents have been incorporated into materials designed to confer a high birefringence on nematic mixtures.[84] The materials are all prepared through convergent syntheses involving palladium-catalyzed cross-coupling reactions. In a demanding case of introducing an aniline group, the Negishi coupling of alkynylzinc reagents **87** and **90**, which can be readily prepared from the terminal alkyne by the deprotonation with butyl lithium and the transmetalation with zinc chloride, had to be used to synthesize liquid crystal molecules **89** and **91** (**Scheme 23**).



Scheme 23. Synthesis of **89** and **91**.

Functionalized azobenzenes were among the first successful nematic liquid crystals used in the display industry. A homologous series of 4-(4-alkylphenylazo)phenols **93**[n] (n = 2–22, even, numbers of the carbon atoms in the alkyl chains) was prepared in yields of 40–70% (**Scheme 24**)[85] by Negishi coupling of alkylzinc chlorides with 4-(4-iodophenylazo)phenol (**92**) under Organ's conditions.[86] The phenols were converted to the corresponding 4-pentylbenzoates **94**[n], which exhibit enantiotropic nematic phases even for **94**[22].

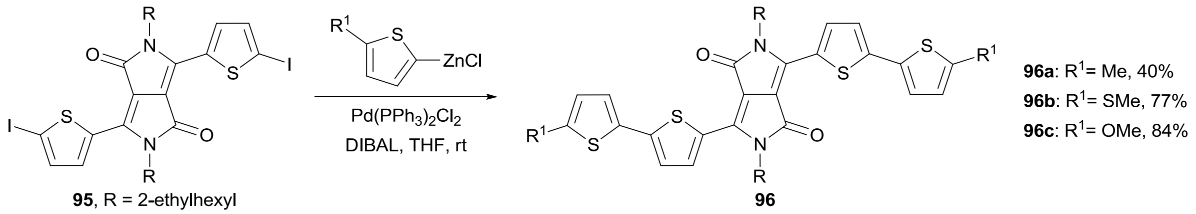


Scheme 24. Synthesis of **94**[n].

3.3 Light-emitting materials

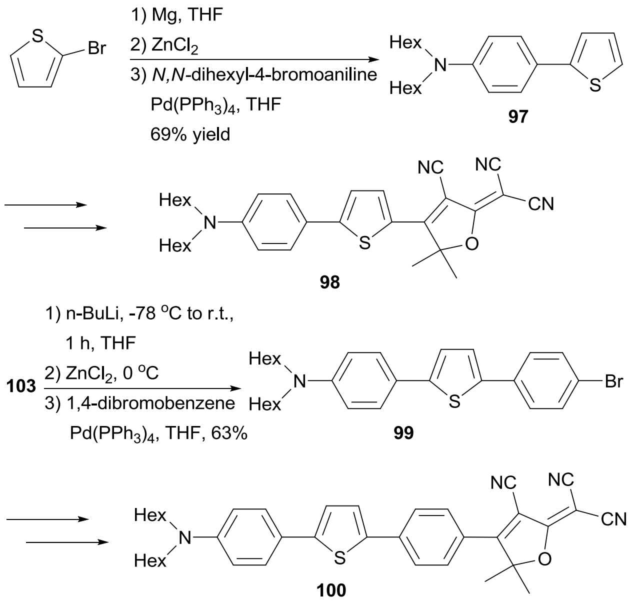
A series of 2,2'-bithiophene-functionalized diketopyrrolopyrrole (DPP) fluorescent dyes bearing different electron-donating and electron-withdrawing substituents at the terminal thiophene units was synthesized by palladium-catalyzed cross-coupling reactions including the Negishi coupling (**Scheme**

25).[87] The diiodide **95** was prepared for the first time in 67% yield by deprotonating the corresponding thiophene-functionalized diketopyrrolopyrrole with LDA (lithium diisopropylamide) followed by the iodinolysis. The cross coupling of **95** with 5-substituted 2-thioenylzinc chlorides give **96a-c**, which display intense red emissions upon photoexcitation in the solution of dichloromethane.



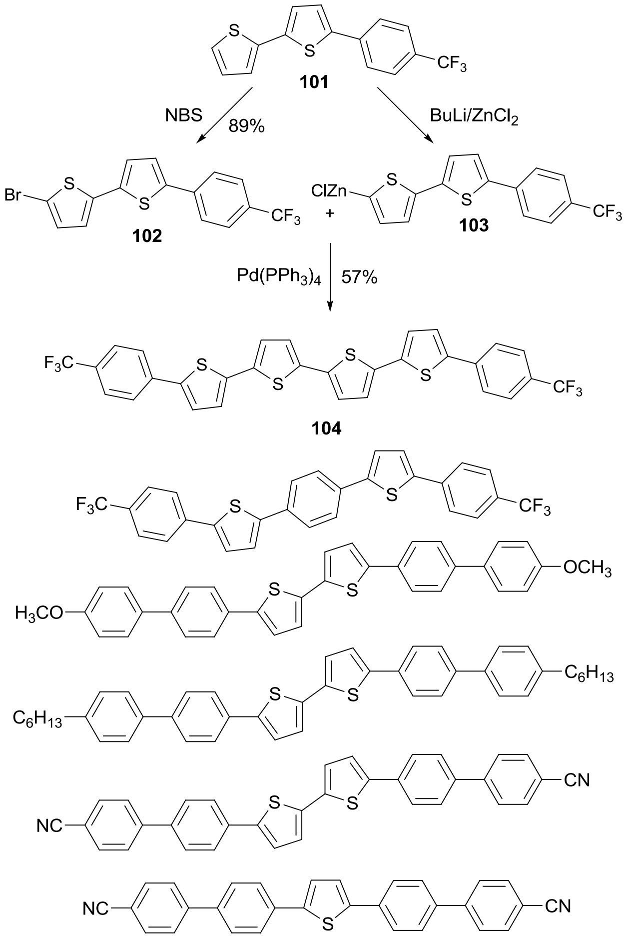
Scheme 25. Synthesis of fluorescent dyes **96a-c**.

Fluorescent dye materials **98** and **100** comprised of an amine donor, a conjugated system, and a dicyanomethylenedihydrofuran acceptor group were synthesized (**Scheme 26**). The conjugated system was constructed by the Negishi coupling.[88] The dye **97** emits in red (λ_{max} = 631 nm) with a high quantum yield of 74%, while compound **100** with extended conjugation emits in deep red ((λ_{max} = 709 nm) with an impressive quantum yield of 34% in toluene.



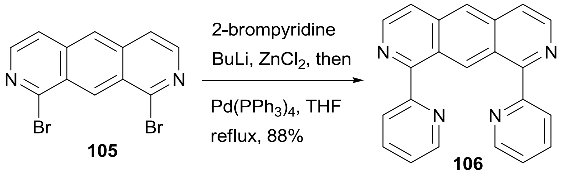
Scheme 26. Synthesis of fluorescent dyes **97** and **100**.

A series of thiophene-phenylene co-oligomers have been synthesized using a Negishi coupling approach,[89] as listed in **Scheme 27**. Some of the syntheses are carried out in a convergent manner. For instance, the bithiophene derivative **101** was brominated to form the bromide **102** and was converted to the organozinc reagent **103**, respectively, and the cross coupling of **102** and **103** to produce the thiophene-phenylene conjugated oligomer **104**.These oligomers can be used in light-emitting transistors.[90]



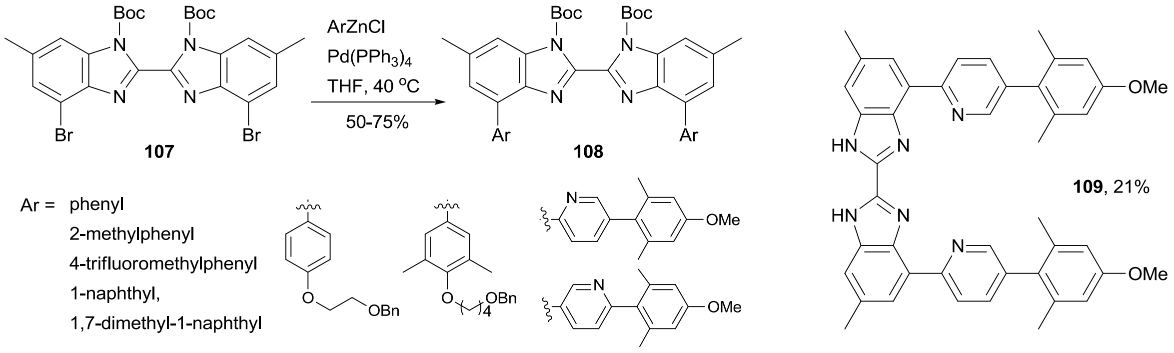
Scheme 27. Convergent synthesis of **104**.

A fluorescent ditopic ligand **106** was synthesized by the cross coupling of 1,8-dibromo-2,7-diazaanthracene **105** with 2-pyridylzinc chloride, which is generated in situ from 2-brompyridine (**Scheme 28**).[91] A successful double cross-coupling reaction requires thoroughly dried zinc chloride (24 h at 55 °C under reduced pressure). Upon irradiation at 366 nm, ligand **106** dimerizes at the 9 and 10 positions to form the head-to-tail tetra-bpy ligand. This thermally stable photodimer can be dissociated back to **106** using higher energy irradiation (254 nm). The photodimerization can be easily monitored by the decrease in the photoluminescence of **106**.



Scheme 28. Synthesis of photodimerizable ditopic ligand **106**.

A series of 4,4'-bisaryl-2,2'-bisbenzimidazoles **108** has been synthesized from the corresponding 4,4'-dibromo-2,2'-bisbenzimidazoles **107** by Negishi coupling reactions (**Scheme 29**).[92] This procedure affords highly substituted bisbenzimidazoles. In the case of cross coupling of **107** with a 2-pyridylzincate, the deprotected form **109** was obtained under the reaction conditions. These bisbenzimidazole-based organic dyes may also serve as multi-dentate ligands for metal complexes.



Scheme 29. Synthesis of 4,4'-bisaryl-2,2'-bisbenzimidazoles **108** and **109**.

The power of the Negishi coupling may be best illustrated by a simple, general procedure developed for the synthesis of a series of fluorescent α-, β-, and γ-substituted bipyridines, terpyridines, phenanthrolines, and pyridylphenanthrolines.[93] The procedure is based on a series of manipulations of palladium-catalyzed cross coupling reactions of organozinc reagents and heteroaryl halides. The method has been showcased with the "manisyl" (4-methoxyl-2,6-dimethylphenyl) group as the aryl prototype (**Figure 1**). Starting from commercially available 3,5-dimethylanisole, 4-methoxy-2,6-dimethylbromobenzene **110-Br** (**110**, X = Br) was prepared according to a literature procedure[94] and then converted into the organozinc reagent **110**-ZnCl. The Negishi coupling of **110**-ZnCl with 2,6-dibromopyridine and 2-bromo-5-iodopyridine gave **111**-Br and **112**-Br, respectively. Cross coupling of **110**-ZnCl with 4-bromopyridine (in the hydrochloride form) to give **113**-H (**113**, X = H), which was converted to **113**-NH_2 (**113**, X = NH_2) under Chichibabin conditions[95] then **113-I** (**113**, X = I) under non-aqueous Sandmeyer conditions.[96] Compounds **111**-Br, **112**-Br, and **113**-I can be converted into their organozinc reagents **111**-ZnCl, **112**-ZnCl, and **113**-ZnCl, respectively.[97] Pairing for the Negishi coupling by choosing one from the four organozinc reagents **110-113**-ZnCl and the other from the aryl halide listed in **Figure 1** including **110-112**-Br and **113**-I creates a large array of ligand patterns (**Figure 1**), which were synthesized in generally satisfactory yields (60-80% in most cases). The compounds emit from ultraviolet to blue light and exhibit quantum yields as high as 87% in acetonitrile. The simplicity and efficiency of the Negishi coupling can hardly be matched by other cross coupling methods in this remarkable approach, especially with the Negishi coupling as essentially the sole player.

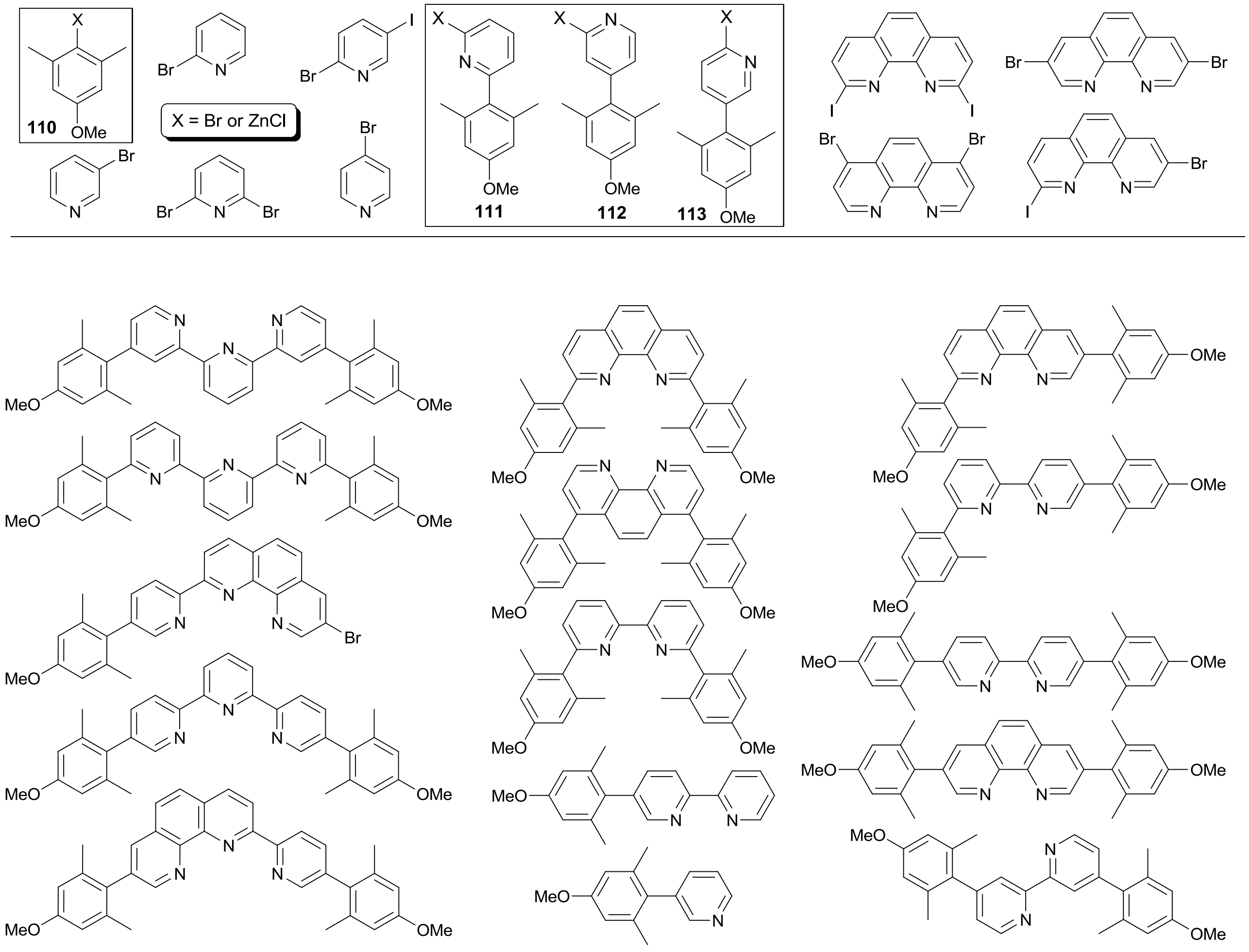
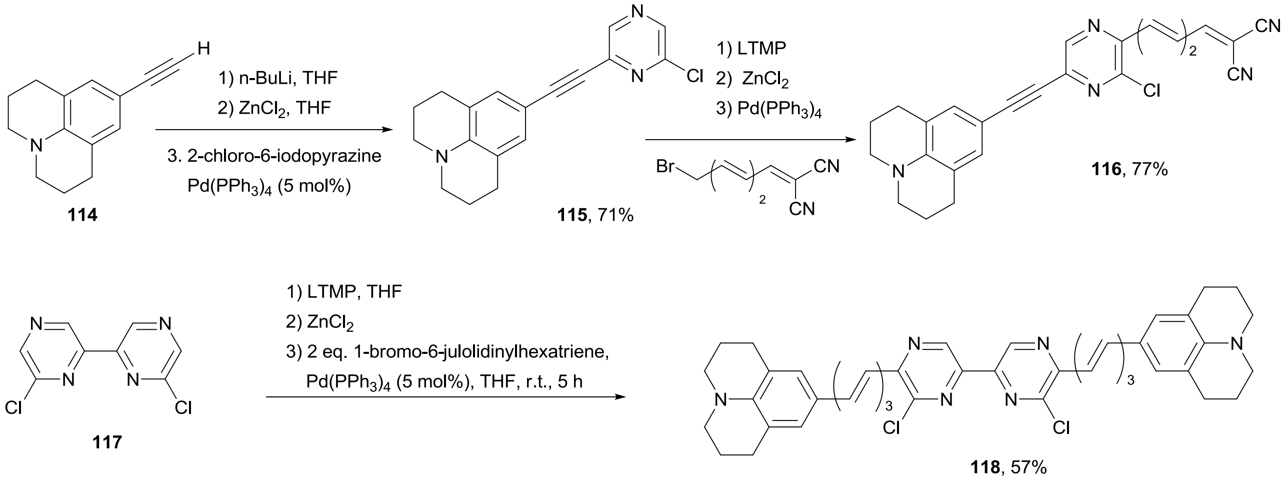


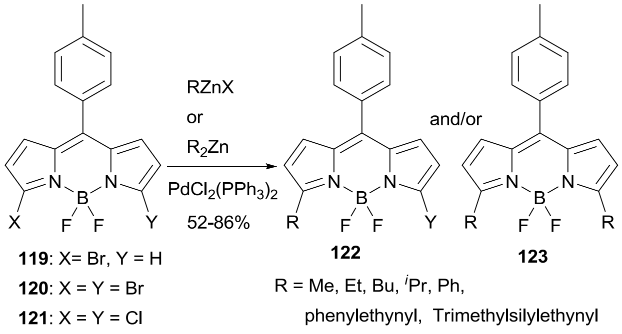
Figure 1. An array of fluorescent ligands made by the Negishi coupling.

Back-to-back Negishi couplings have been used to prepare push-pull molecule **116** with extended conjugation (**Scheme 30**).[98] Terminal alkyne **114** was first converted to the corresponding zinc reagent then cross coupled with 2-chloro-6-iodopyrazine chemoselectively to produce **115** in good yield. Compound **115** was selectively deprotonated with LTMP and converted to the zinc reagent, which reacted with (3*E*,5*E*)-6-Bromo-1,1-dicyanohexa-1,3,5-triene to give **116** in good yield. Two-fold Negishi coupling is required for the synthesis of **118** from 6,6'-dichloro-2,2'-bipyrazine (**117**). These molecules exhibit emissions in near infrared region (707-744 nm). They also absorb strongly blue to orange visible lights.



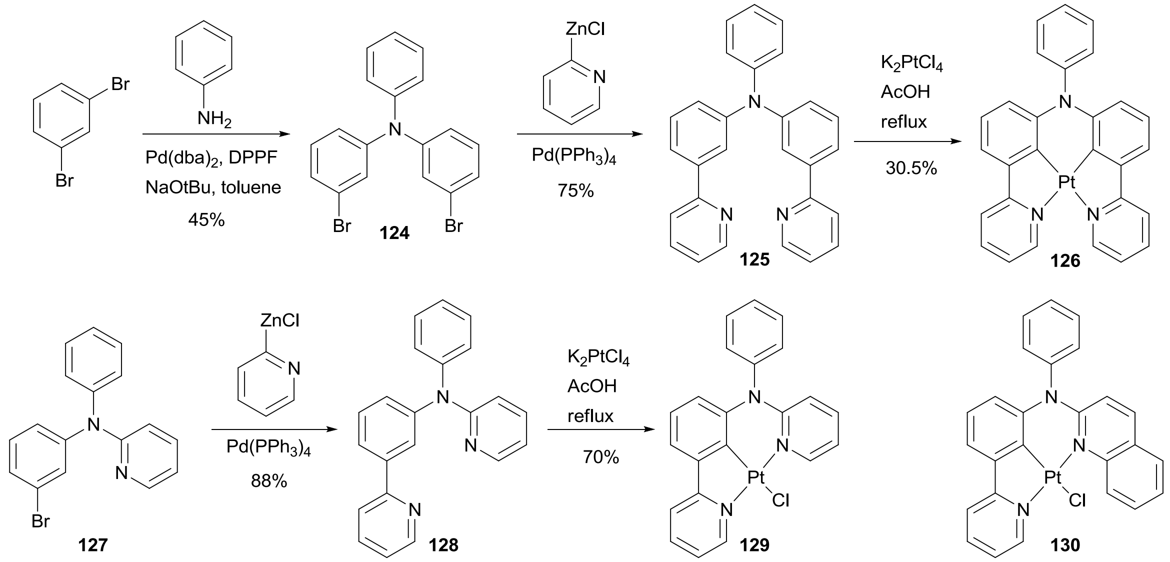
Scheme 30. Synthesis of near infrared fluorescent dyes **116** and **118**.

BODIPY (boron dipyrrin or boron dipyrromethene) dyes constitute one of the most important families of luminophores, due to their easily tunable absorption and emission properties.[99] BODIPY dyes have very broad photonic applications such as sensors, laser dyes, photodynamic therapy, OLEDs and solar cells. A recent study shows that the Negishi coupling is a promising tool for modifying BODIPY dyes.[100] 3-Bromo, 3,5-dibromo, and 3,5-dichloroBODIPYs, **119**, **120**, and **121**, respectively, reacted smoothly with various organozinc reagents in the presence of $PdCl_2(PPh_3)_2$ to give the 3,5-substituted BODIPY derivatives (**Scheme 31**). Control of the reaction to obtain monosubstituted products from both **120** and **121** is possible, which allows the introduction of two different groups at the 3- and 5-positions. Most of the reactions gave satisfactorily high yields except for the benzylation, which took place with low yield of 20%. A modified ligand may be required in this demanding case.



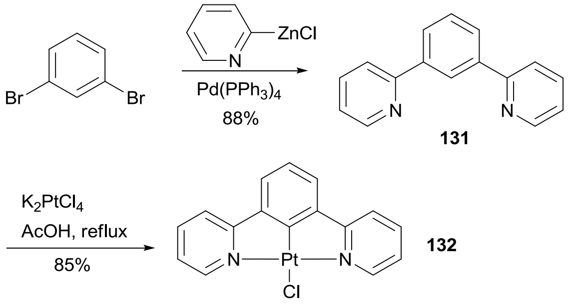
Scheme 31. Modification of BODIPs using the Negishi coupling.

Phosphorescent materials based on transition metal complexes have recently attracted a great deal of attention because of their various applications in chemical, biological, and in particular as triplet emitters in OLED devices.[101] The ligands for these complexes are typically conjugated aromatic and/or heteroaromatic assemblies that can be easily constructed by palladium-catalyzed cross coupling reactions. Huo and coworkers have designed and synthesized several types of tridentate and tetradentate cyclometalating ligands. The platinum complexes based on these ligands possess a less common five-six-membered metallacycle, and display high photoluminescence quantum yields in dichloromethane at room temperature.[102-106] Their application to OLED devices has been demonstrated.[102] An efficient synthetic strategy based on the combination of palladium catalyzed C–C and C–N bond cross coupling reactions was developed to synthesize these cyclometalating ligands. As illustrated in **Scheme 32**, the Negishi coupling of 2-pyridiylzinc chloride with dibromide **124** efficiently installs two pyridyl groups to give **125**, which reacts with K_2PtCl_4 as a tetradentate cyclometalating ligand to form red emitting complex **126**.[102] Ligand **128** for highly luminescent platinum complex **129** was also prepared from **127** using the Negishi coupling, and similar approach was applied to the synthesis of orange emitter**130**.[104]



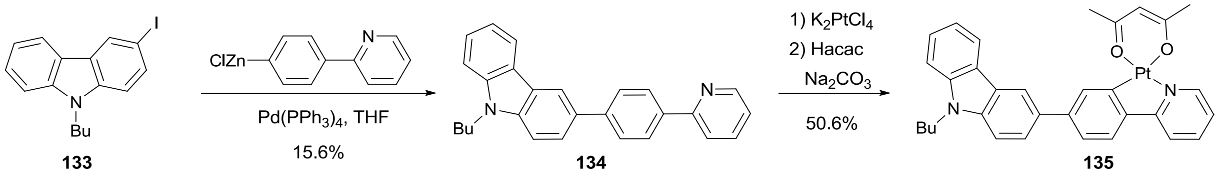
Scheme 32. Synthesis of cyclometalating ligands **125** and **128**.

Complex **132**[107] is a prototype in the family of highly luminescent N^C^N-coordinated platinum complexes and has been used as an triplet emitter in OLED devices showing high quantum efficiency.[107c] The synthesis of ligand **131** originally relied upon the Stille coupling of the 1,3-dibromobenzene with a 2-pyridylstanne reagent,[107a] however, recent reports demonstrated that the Negishi coupling is a much better choice to construct this ligand and most likely its analogues as well (**Scheme 33**).[107c,108]



Scheme 33. Synthesis of **131**.

Zhao and coworkers[109] synthesized a carbazole-capped cyclometalated platinum(II) complex **135** used in an oxygen sensor. The bidenate ligand **134** is synthesized by the Negishi coupling of **133** with the 4-(2-pyridyl)phenylzinc chloride generated from the corresponding bromide as shown in **Scheme 34**.

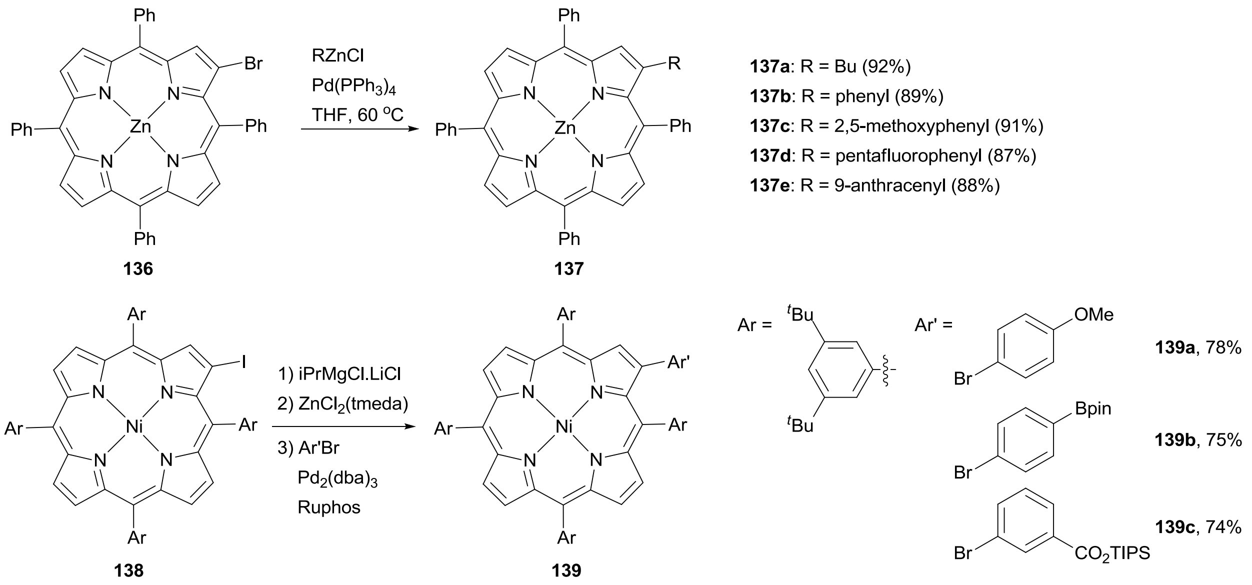


Scheme 34. Synthesis of bidentate ligand **134**.

3.4 Light-harvesting materials

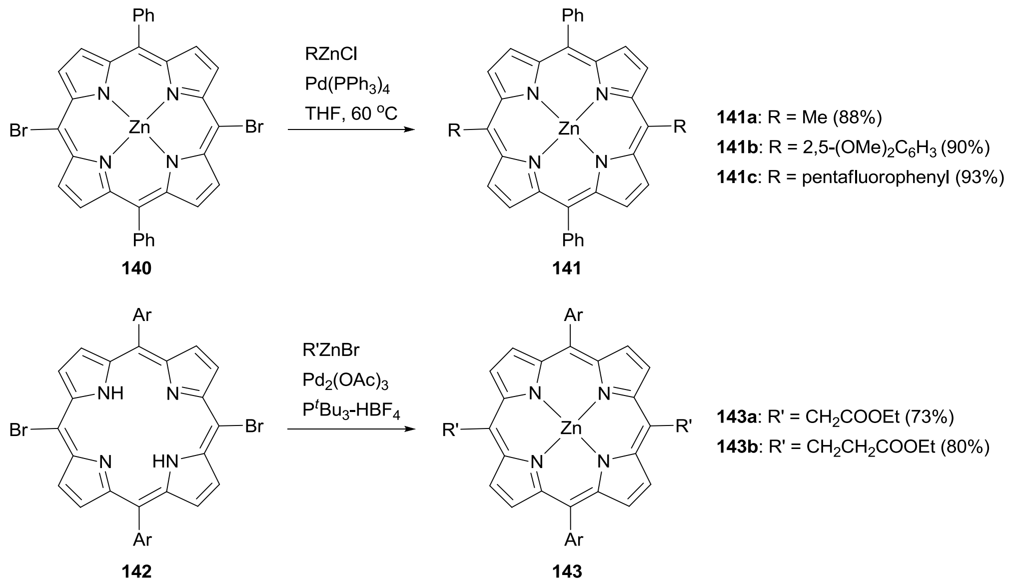
Porphyrins are important macrocyclic heteroaromatic compounds and play various important roles in nature, particularly in photosynthesis. They are commonly used as building blocks in supramolecular chemistry and recently as a light harvesting component in dye-sensitized solar cells (DSSCs).[110] One of the easiest ways to modify porphyrins is to substitute at their periphery positions and the Negishi coupling has proved to be an efficient tool for such trasformation.[111-114]

Functionalization at a β-position of porphyrins using the Negishi coupling was first reported by Therien and co-workers.[111] The β-bromoporphyrin **136** reacted with either butyl or arylzinc chloride in the presence of Pd(PPh$_3$)$_4$ to give the β-substituted product **137** in excellent yields (**Scheme 35**). More recently, a different approach was adopted by generating the zinc reagent from iodoporphyrin **138**, which cross coupled with aryl bromides to give **139** in high yields.[114]



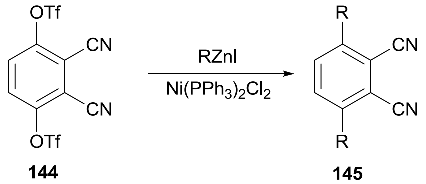
Scheme 35. Negishi coupling at the β position of porphyrins.

Modification at the *meso*-position by the Negishi coupling has also been demonstrated. The reaction of meso-dibromo-substituted porphyrin **140** with methyl, 2,5-dimethoxyphenyl, and pentafluorophenylzinc chlorides produced **141a-c**, respectively, in excellent yields.[111b] Takanami and co-workers introduced various functionalized alkyl and aryl groups to the meso positions of free porphyrin ligands.[112a] For instance, the reaction of **142** with functionalized alkylzinc bromides gives **143** in high yields (**Scheme 36**). In addition, they also reported an interesting cyanation at the β or meso position of porphyrins via palladium catalyzed cross coupling of 2-cyanoethylzinc bromide with β or meso-bromophorpyrin. 2-Cyanoethylzinc bromide serves as the cyanide source.[112b]



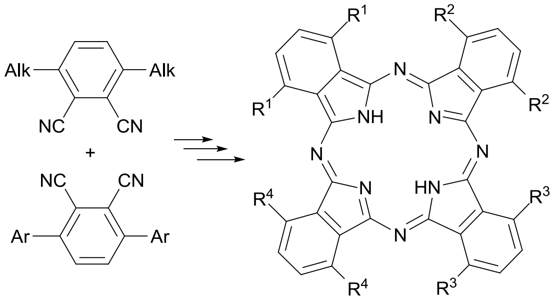
Scheme 36. Negishi coupling at the meso positions of porphyrin.

Phthalocyanines, structurally similar to porphyrins, are another family of optically important compounds having found applications in solar cells, photodynamic therapy, optical data storage and being used as nonlinear optical and optical limiting materials. With Negishi coupling, a series of precursors **145** for the synthesis of phthalocyanines **146** can be prepared from the bis-triflate derivative **144**.[115-117] The inexpensive $NiCl_2(PPh_3)_2$ was used as the effective catalyst for this transformation. The Suzuki coupling with in situ generated tridecylborane to introduce the alkyl group was reported to give the desired product in much lower yields (~30%) under various conditions including using $PdCl_2$(dppf) as the catalyst and K_3PO_4 or K_2CO_3 as the base.[117]



144 **145**

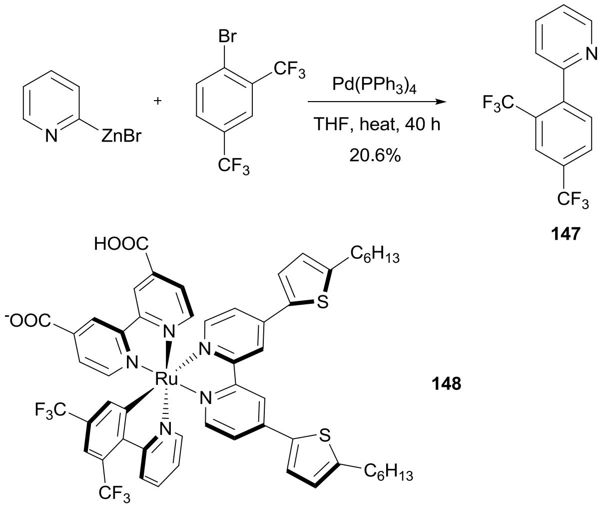
R	Yield %	R	Yield %
pentyl	56	chlorohexyl	61
hexyl	68	4-pivaloylbutyl	62
decyl	70	S-3,7-dimethyloctyl	68
3-methylbutyl	72	4-methoxyphenyl	67
4-methylbutyl	69	3-methoxyphenyl	66
5-methylpentyl	63	2-methoxypphenyl	30
cyclopentylmethyl	45	1,1-H-2,2-H-perflurodecyl	58
cyclohexylmethyl	41		



146: R^1, R^2, R^3, R^4 = alkyl or aryl groups

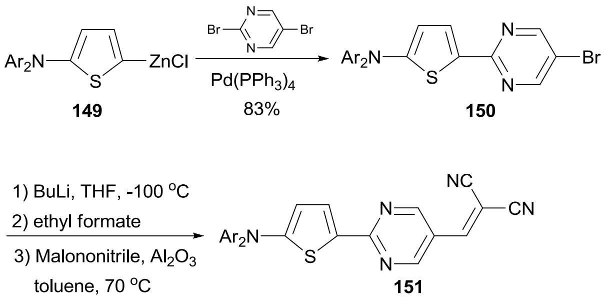
Scheme 37. Synthesis of phthalocyanines' precursors **145**.

Dye sensitized solar cells (DSSCs) offers a promising alternative to conventional photovoltaic technologies. A tris-heteroleptic cyclometalated Ru(II) sensitizer **148** is prepared, which demonstrates high power output in a DSSC with a performance of 7.3% (η) under AM1.5 irradiation and 8.3% at half of that light intensity. The cyclometalating ligand **147**, was prepared by a Negishi coupling of 2-pyridylzinc bromide and 1-bromo- 2,4-bis(trifluoromethyl)benzene (**Scheme 38**).[118]



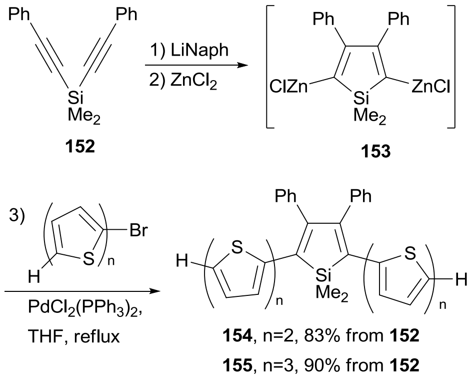
Scheme 38. Synthesis of cyclometalating ligand **147**.

A donor-acceptor-acceptor molecule suitable for vacuum-processing was synthesized by three steps of reactions as shown in **Scheme 39**.[119] First, palladium-catalyzed coupling reaction of the organozinc reagent **149** derived from 2-(N,N-di-(p-tolyl)amino)thiophene with 5-bromo-2-iodopyrimidine afforded **150**, which was then converted to the corresponding carbaldehyde by lithiation with butyllithium and subsequently quenching with ethyl formate. Finally, the aldehyde was condensed with malononitrile to yield the target compound **151** via the Knöevenagel reaction in the presence of basic aluminium oxide. When compound **151** was used as the donor material in a vacuum-deposited planar-mixed heterojunction solar cells with C70 as the acceptor, power conversion efficiency as high as 6.4% was achieved.



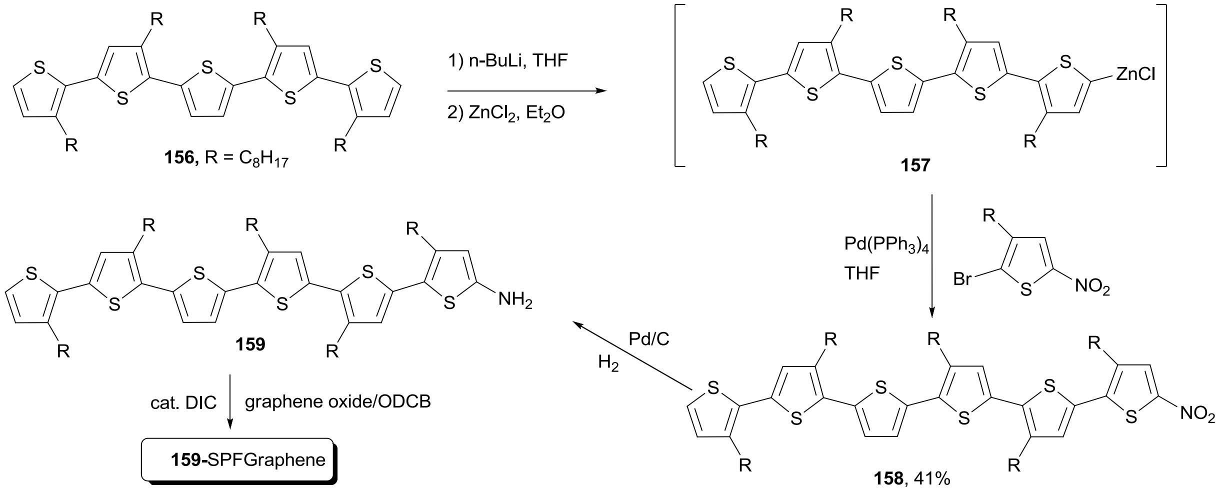
Scheme 39. Synthesis of **151**.

A series of donor-acceptor materials based on polythiophene modified with silole moieties were prepared by electrochemical anodic polymerization of 2,5-bis([2,2′-bithiophen]-5-yl)-1,1-dimethyl-3,4-diphenylsilole (**154**) and 2,5-bis([2,2′-terthiophen]-5-yl)-1,1-dimethyl-3,4-diphenylsilole (**155**), as well as copolymerization of these monomers with 2,2′-bithiophene, and their electrochemical and photovoltaic properties were investigated.[120] The required electrochemically active monomers **154** and **155** are prepared by the one-pot, three-step methodology involving Tamao's reductive cyclization[121] of **152** with lithium naphthlenide (LiNaph), transmetalation with $ZnCl_2$, and Negishi cross coupling of the resulted organozinc reagent **153** (**Scheme 40**).



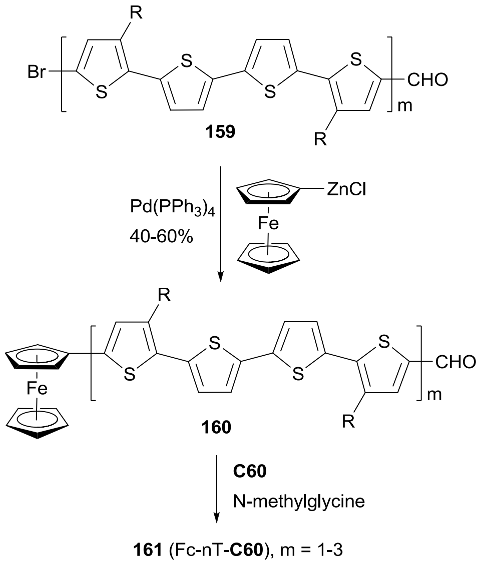
Scheme 40. Synthesis of **154** and **155**.

Functional oligothiophenes are frequently used π-conjugated materials as active components in organic electronic devices and molecular electronics.[122] Oligothiophene **158** was prepared by utilizing Negishi cross-coupling reaction of **157** with 2-bromo-5-nitro-3-octylthiophene, which, after hydrogenation reduction of the nitro group, was covalently bonded to the graphene to form the oligothiphene-graphene nanohybrid **159**-SPFGraphene (**Scheme 41**)[123]. The attachment of the electron-acceptor group (graphene oxide sheet) onto the oligothiophene molecules results in an improved absorption compared with its parent compound in the whole spectral region and an efficient quenching of photoluminescence. This modified graphene shows superior solution processability and better optical limiting effect than the benchmark optical limiting material C60.[123]



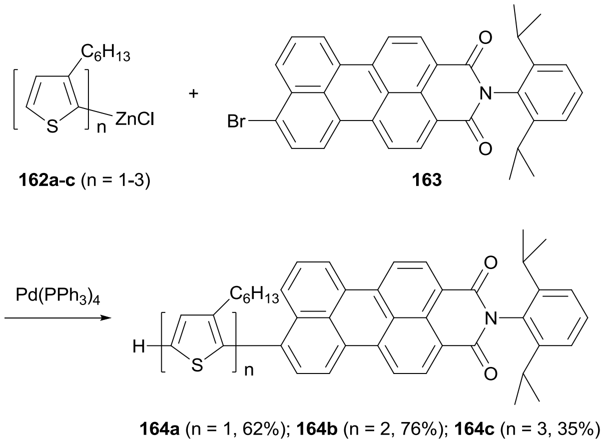
Scheme 41. Synthesis of **159**-SPFGraphene.

A strongly electron-donating ferrocenyl group is introduced into the oligothiphenes **159** (m= 1-3) by a Negishi coupling of ferrocenylzinc chloride. The ferrocene substituted derivatives **160** (m= 1-3) are covalently bonded to C60 to form the ferrocene-oligothiophene-fullerene triads **161**(Fc-nT-C60, m= 1-3) (**Scheme 42**).[124] In the triads, the conjugation between the ferrocene and the oligothiophene serves to promote electron transfer either from the excited oligothiophene to the fullerene or from the oligothiophene to the excited fullerene. The Negishi coupling was also used to attach 3,4-ethylenedioxythiophene (EDOT) moiety to a core structure of heptacyclic polyarene 10,15-dihydro-*5H*-di-indeno[1,2-*a*;1’,2’-*c*]fluorene (truxene, Tr) and elongate the thiophene moiety in the synthesis of star-shaped D-π-B-A derivatives end-capped with pyrrolidino fullerene.[125] These compounds can be used as potential light-harvesting materials in solar cell devices.



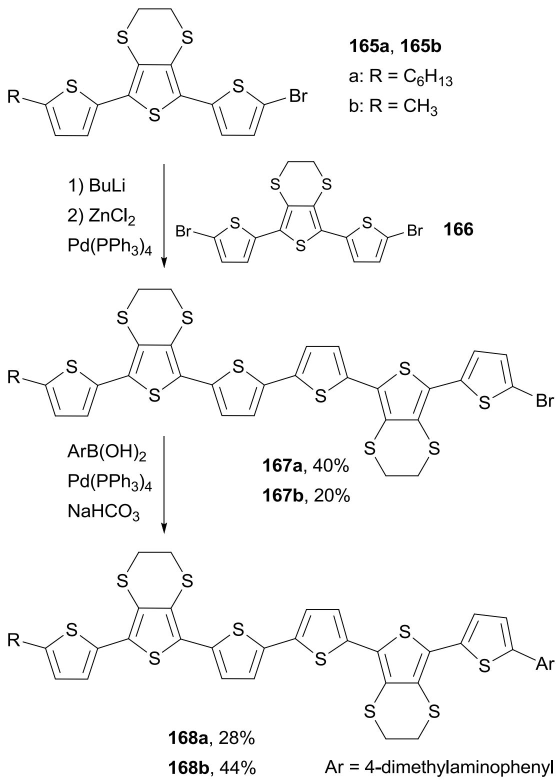
Scheme 42. Synthesis of triads **161** (Fc-nT-C60).

A series of donor–acceptor systems, consisting of head-to-tail coupled oligo(3-hexylthiophene)s covalently linked to perylenemonoimide are created *via* effective palladium-catalyzed cross-coupling reactions of **162a-c** with **163** in good to excellent yields (**Scheme 43**).[126] The synthesized perylenyl–oligothiophenes **164a-c** display a strong absorption between 300 and 550 nm and a nearly complete fluorescence quenching of the perylene acceptor. Furthermore, the HOMOs of these hybrid compounds are lower than the work function of a PEDOT-coated ITO electrode, and their LUMOs are higher than both the LUMO of fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and the work function of aluminum cathode, which makes them suitable light-harvesting materials for applications in photovoltaic devices.[126]



Scheme 43. Synthesis of **164a-c**

Skabara and co-workers prepared sexithiophenes **168a** and **168b** with a 4-(dimethylamino)phenyl end-capping group by using a combination of the Negishi and the Suzuki couplings.[127a] The mono brominated terthiophene intermediate **165** is converted to the corresponding organozinc reagent, which cross-couples with the dibrominated terthiophene **166** to give **167**. The second step involves the Suzuki coupling of **167** with 4-(dimethylamino)phenylboronic acid, giving sexithiohenes **168**. Compared with similar sexithiophenes with both ends capped symmetrically with a hexyl or methyl group, which have been used as the electron donor material in a bilayer photovoltaic device,[127b] the introduction of the end-capping 4-(dimethylamino)phenyl group in **168a** and **168b** lowers the band gap and shifts the absorption to longer wavelength by about 10 nm. The Sexithiophenes are also efficient luminescence quenchers of quantum dots.[127a]

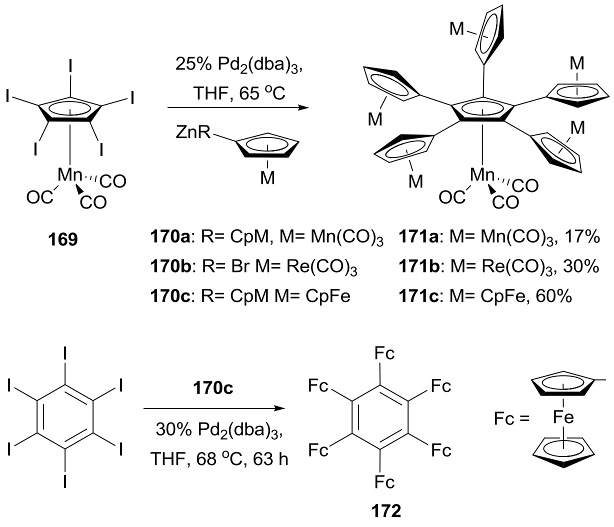


Scheme 44. Synthesis of **168a** and **168b**.

4. Electrochemical materials

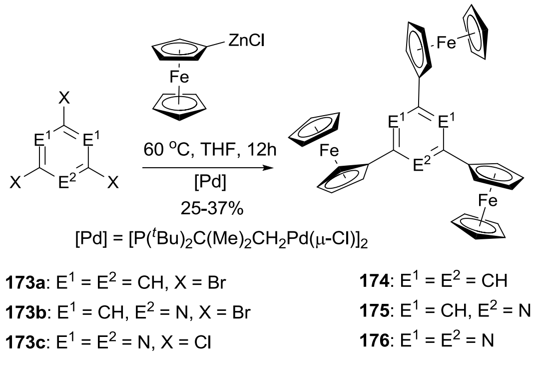
Electrochemical materials discussed here are referred as those displaying unique electrochemical properties such as reversible and stable multiple electron redox processes, which may be used in advanced organic electronic and optical devices, energy storage devices, redox-responsive sensors, and catalysis. Multinuclear metallocene complexes have various applications from molecular electronics to homogenous catalysis. Owing to its electron-richness, ferrocene (Fc) undergoes a one-electron oxidation to form stable ferrocenium ion (Fc+) at a low potential. This process is reversible, making ferrocene a commonly used standard in electrochemistry. Molecules with multiple ferrocenyl groups are particularly attractive, mainly because of their unique redox properties and electrochemical stability. They can be used as multi-electron redox catalysts, electron storage devices, and the surface modifiers of electrodes.

There is a tremendous effort to construct a π-conjugated system with multiple ferrocenyl motifs, so that the electronic communication between ferrocenyl centers can be assessed. Star-shaped two-dimensional oligoferrocene derivatives with directly connected metallocene fragments are expected to have optimal electronic communication between the metal centers as found in the linear poly(ferrocenes).[128] However, the synthesis of such an oligoferrocene was a challenge until the first synthesis of radial oligocyclopentadienyl metal complexes **171a-c** in 2006 by Vollhart and co-workers[129] (**Scheme 45**). After extensive experimentation with various cross-coupling reagents,[130] they found that a five-fold Negishi coupling turned out to be the most efficient tool to introduce multiple metallocenyl groups to an aromatic core. As shown in **Scheme 45**, the reaction of metallocenyl zinc reagents **170a-c** with $[Mn(C_5I_5)(CO)_3]$ **169** gave the sexicyclopentadienyl metal complexes **171a-c**, respectively, in satisfactory yields. Electrochemical investigation of the ferrocene derivative **171c** revealed three separate redox waves corresponding to a single one-electron transition (half-wave potential $E_{1/2}$ = 5mV vs Fc/Fc^+) and a pair of two-electron transitions ($E_{1/2}$ = 169, 282 mV), indicating some intramolecular electronic communication between the metal centers. Sterically more congested hexaferrocenylbenzene **172** was also prepared, for the first time, by the Negishi coupling of **170c** with hexaiodobenzene in 4% yield, while pentaferrocenylbenzene was isolated in 56% yield.[131] The use of hexabromobenzene is less effective in forming highly ferrocenylated benzene. Three clearly separated redox waves, a single one-electron ($E_{1/2}$ = -162.8 mV vs Fc/Fc^+), a two-electron (-32.3 mV), and a three-electron transition (222.4 mV), were observed from the voltammogram of **172**.



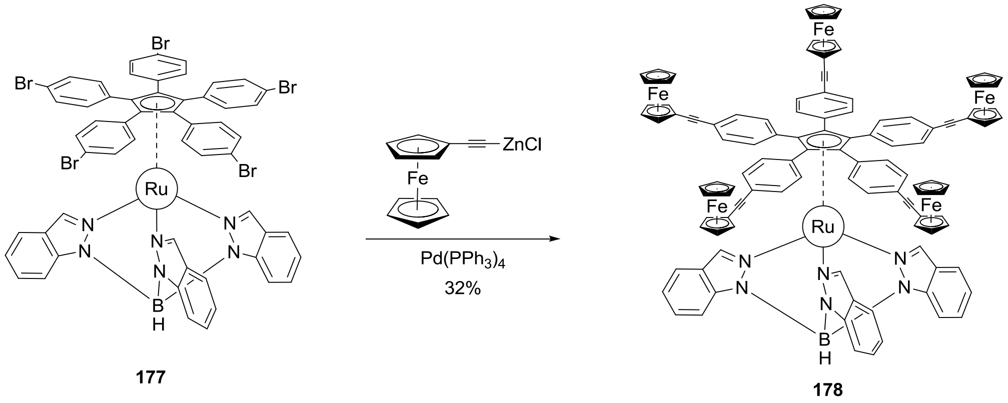
Scheme 45. Synthesis of sexicyclopentadienyl metal complexes **171a-c** and hexaferrocenylbenzene **172**.

A series of di- and triferrocenyl (hetero)aromatics are prepared using the Negishi C–C cross-coupling of ferrocenylzinc chloride with multi halogenated heteroarenes.[132] 1,3,5-Triferrocenylbenzene (**174**), 2,4,6-triferrocenylpyridine (**175**), and 2,4,6-triferrocenyl-1,3,5-triazine (**176**) were synthesized by the reaction of ferrocenylzinc chloride with **173a-c**, respectively (**Scheme 46**).Three well-defined, separated by140 −185 mV ($\Delta E_{1/2}$, difference in the individual half-wave potential), and reversible one-electron processes were observed for **174**−**176**, pointing to weak intermetallic interactions.



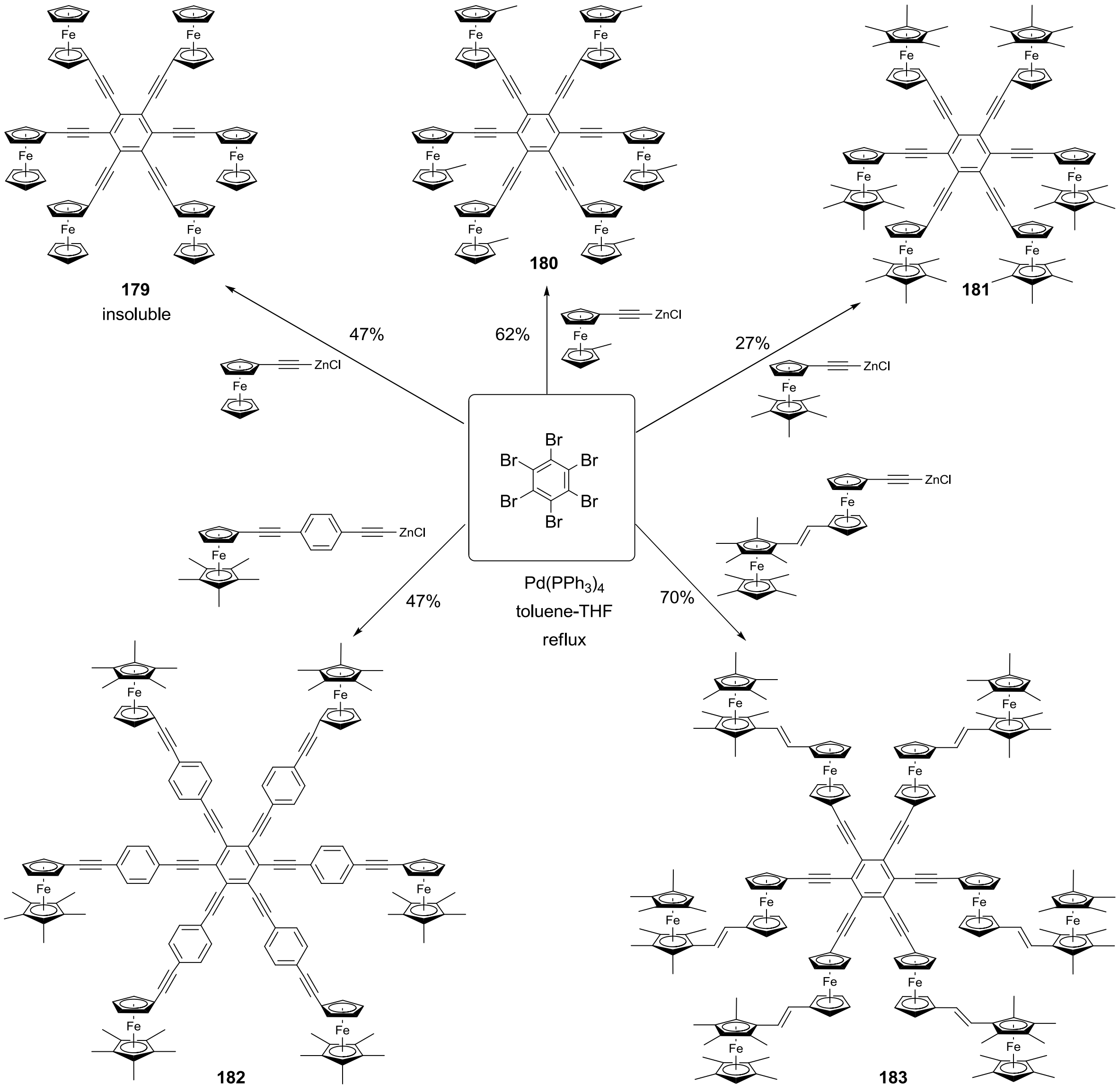
Scheme 46. Synthesis of triferrocenyl(hetero)arenes **174-176**.

The redox activity of the ferrocenyl group has been incorporated into the concept of redox-driven single molecular motor.[133] The rotor **178** composed of five terminal electroactive groups has been prepared and connected to a tripodal ligand (stator) by means of a ruthenium(II) center (**Scheme 47**). The five ferrocenyl groups were introduced by the coupling of ferrocenylethynylzinc chloride with ruthenium (II) complex **177** as shown in **Scheme 47**. Attempts under Sonogashira conditions with various catalysts and phosphines, including even the very bulky and electron-rich tris(tert-butyl)phosphine, failed. This system can be considered as the heart of a future molecular motor, since it is particularly well-suited for the preparation of a family of molecules through variations of the hydrotris(indazolyl) borate ligand. The stator can be functionalized to allow its deposition on various surfaces.



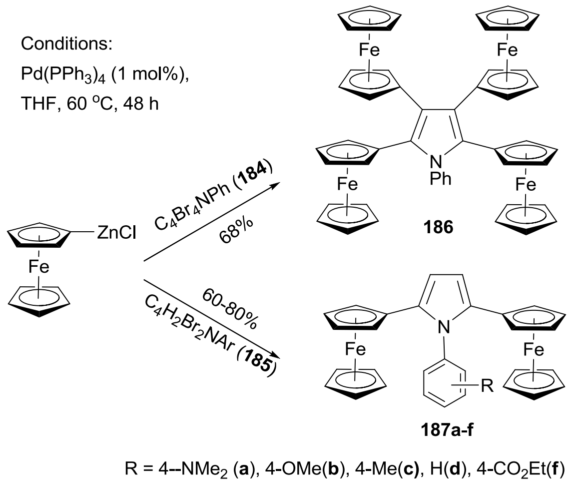
Scheme 47. Synthesis of molecular motor **178**.

Astruc and coworkers have synthesized a family of rigid redox stars **117-183** by the Negishi coupling of hexabromobenzene with various alkynylzinc reagents (**Scheme 48**).[134,135] Once again, attempts to use the Sonogashira coupling failed to produce desired hexasubstituted products. Cyclic voltammetry studies show that these compounds display a single wave for the six-electron oxidation when using NBu_4PF_6 as the supporting electrolyte, whereas splitted multiple electron transfer processes are observed when NBu_4BAr_4 (Ar = 3,5-bistrifluoromethylphenyl) is used as the supporting electrolyte. This, in combination with the study of other closely related family members of rigid ferrocenyl-terminated redox stars, confirms the lack of electronic communication between the redox centers and a significant through-space electrostatic effect among the oxidized ferrocenyl groups.[134, 135]



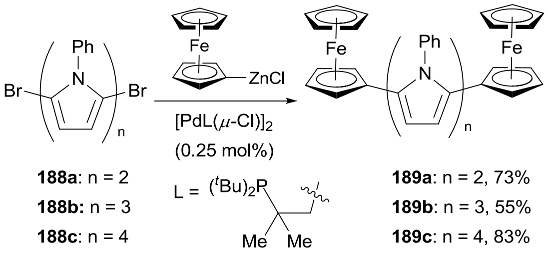
Scheme 48. Synthesis of redox stars 179-183 by six-fold Negishi coupling.

Recently, Lang and co-workers have used the Negishi coupling to introduce ferrocenyl groups to the peripheries of pyrrole, furan, and thiophene cores.[136-140] Tetraferrocenyl pyrrole **186** was synthesized by the palladium catalyzed cross coupling of ferrocenylzinc chloride with 2,3,4,5-tetrabromo-1-phenyl-1H-pyrrole (**184**) in 68% percent yield.[136] Under the same conditions, di-ferrocenylpyrrole **187a-f** with various substituents on the N-phenyl ring were prepared from 2,5-dibromo-1-aryl-1*H*-pyrrole (**185**) in high yields (**Scheme 49**).[137] Similar compounds with a furan or thiophene core were also prepared using the similar Negishi coupling.[138] Compound **186** displays four reversible one-electron transfer processes with remarkably high $\Delta E_{1/2}$ values and reduction potentials of E^{0f} = –280, 51, 323, and 550 mV ($\Delta E_{1/2}$ = 322, 264, and 233 mV) using $[NBu_4][B(C_6F_5)_4]$ as the supporting electrolyte.[136] Compounds **187c** displayes two electrochemically reversible one-electron transfer processes with even higher $\Delta E_{1/2}$ value and reduction potentials of E^{0f} = –238 and E^{0f} =212 mV ($\Delta E_{1/2}$ = 450 mV). These results, compared with those from other ferrocenyl substituted aromatic and heteroaromatic compound described previously, suggest a strong intermetallic communication between ferrocenyl and ferrocenium termini when using a pyrrole as the connecting unit. The substituents on the phenyl ring of compound **187a-f** has an influence on both the redox potentials and the separation of the redox potentials, with electron-donating groups (**187a-c**) increasing the $\Delta E_{1/2}$ values, while the electron-withdrawing groups (**187e** an **187f**) decreasing the redox separation.[137] A total of 13 thiophene derivatives with one to five ferrocenyl groups substituted at the periphery positions of thiophene are prepared by the Negishi coupling using ferrocenylzinc chloride in generally satisfactory yields.[139] Ferrocenyl-substituted thiophenes also display redox separations, but not as large as those displayed by their pyrrole counterparts.



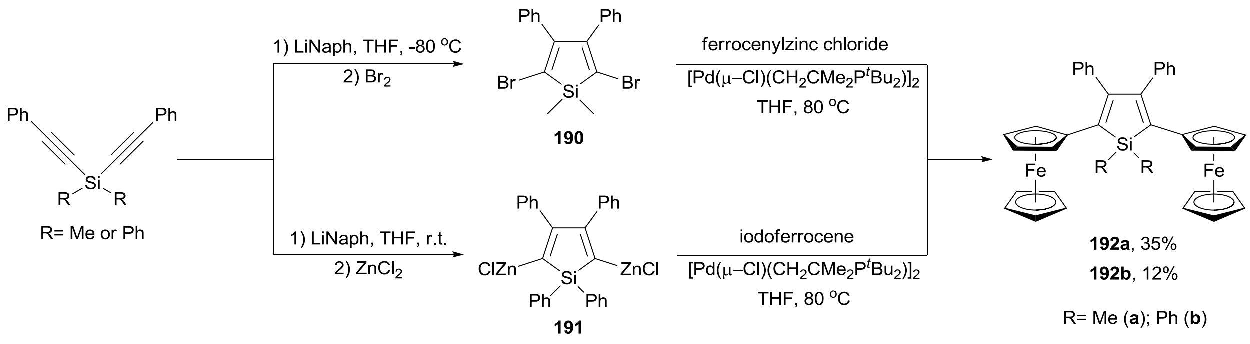
Scheme 49. Synthesis of **186** and **187a-f**.

The large redox separation displayed by compounds **187a-f** suggests that the pyrrole is an excellent connecting unit for two ferrocenyl centers allowing efficient electronic interaction between the two redox centers, which implies a possible model for molecular wires containing oligo(pyrrole) units. To this end, a series of oligopyrroles **188a-c** were prepared by the iterative alternation of bromination and Negishi coupling of the corresponding pyrrolyl derivatives, which were capped by two ferrocenyl groups through Negishi coupling again with ferrocenylzinc chloride to form molecular wires **189a-c** (**Scheme 50**).[140] The redox splitting is decreased as the number of pyrrole units increases, and the ferrocenyl moieties in quarterpyrrole **189c** are oxidized simultaneously.



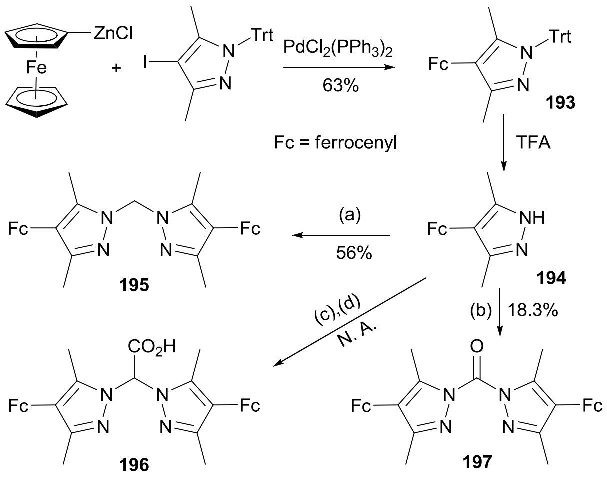
Scheme 50. Synthesis of ferrocene capped oligopyrroles **189a-c**.

Ferrocenyl-substituted siloles **192a** and **192b** are both prepared by the reductive cyclization of dialkynylsilanes and subsequent Negishi coupling but with different strategies (**Scheme 51**).[141] Silacyclopentadiene **190** was prepared by the reductive cyclization of dimethylbis(phenylethynyl)silane followed by bromination. Cross coupling of the dibromide with ferrocenylzinc chloride gave **192a** in 35% yield. For the synthesis of **192b**, the organozinc reagent **191** had to be used to couple with iodoferrocene since the other combination did not work. Interestingly, compounds **192a** and **192b** undergo two sequential ferrocenyl-based redox processes with the separations of 300 and 280 mV ($\Delta E_{1/2}$), respectively, which are similar to that displayed by diferrocenylfuran ($\Delta E_{1/2}$ = 290 mV).[141]



Scheme 51. Synthesis of ferrocenyl-substituted siloles **192a** and **192b**.

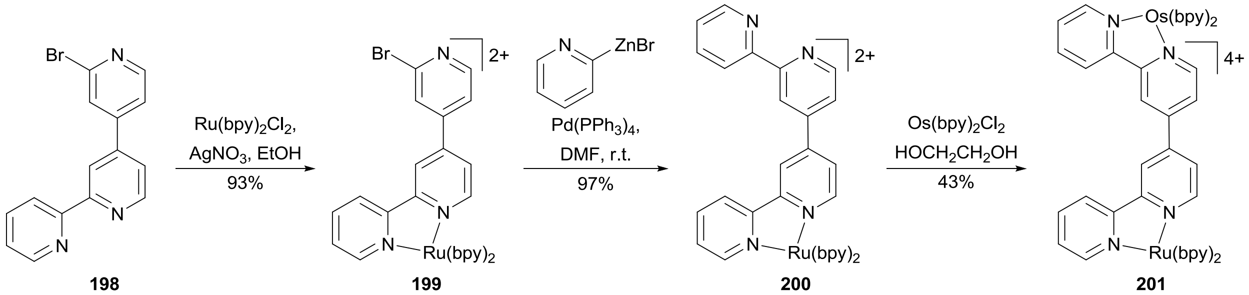
The compound 4-ferrocenyl-3,5-dimethylpyrazole (**194**) is synthesized from 4-iodo-3,5-dimethyl-1-tritylpyrazole via a Negishi cross-coupling reaction[142] and subsequent deprotection of the intermediate **193**.[143] From **194**, chelating ligands **195-197** are prepared under various conditions (**Scheme 52**). The redox properties and complexation of **196** with iron were studied. Ligands **195** and **196** were suggested for future model complexes by mimicking the redox processes of Rieske dioxygenases.



Conditions: (a) KOH, K_2CO_3, CH_2Cl_2, TEBAC; (b) NEt_3, triphosgene;
(c) Br_2CO_2H, KO^tBu, TEBAC; (d) H_2O, HCl.

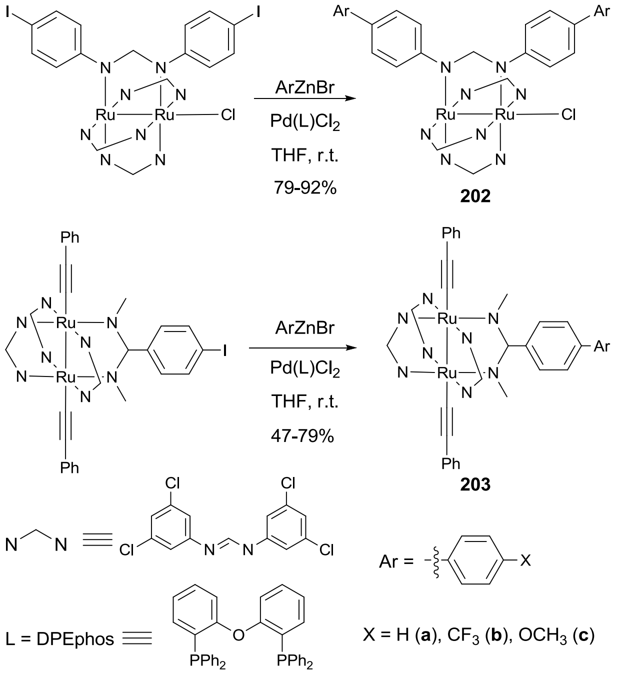
Scheme 52. Synthesis of **193**.

The Negishi coupling has been used to create a new binding site in a complex resulting in a heterodimetallic ruthenium-osmium complex (**Scheme 53**).[144] Ligand **198** was prepared in high yield by the cross coupling of 2,2'-dibromo-4,4'-bipyridine with 2-pyridylzinc bromide (2 equivalents) at room temperature in THF with $Pd(PPh_3)_4$ as the catalyst. The high yield of the mono cross-coupled product **198** is due to the precipitation of its $ZnBr_2$ complex from the reaction mixture. The zinc bromide can be sequestered by treating the complex with EDTA. The reaction of **198** with $RuCl_2(bpy)_2$ (bpy = 2,2'-bipyridine) gives **199**. Complex **199** reacted with excess 2-pyridylzinc bromide in the presence of the palladium catalyst to form **200** almost quantitatively, which was converted to the heterodinuclear complex **201** by reacting with $OsCl_2(bpy)_2$. The oxidation of the osmium metal center does not alter the oxidation potential of the ruthenium metal center, indicating weak metal-metal interaction in these complexes.



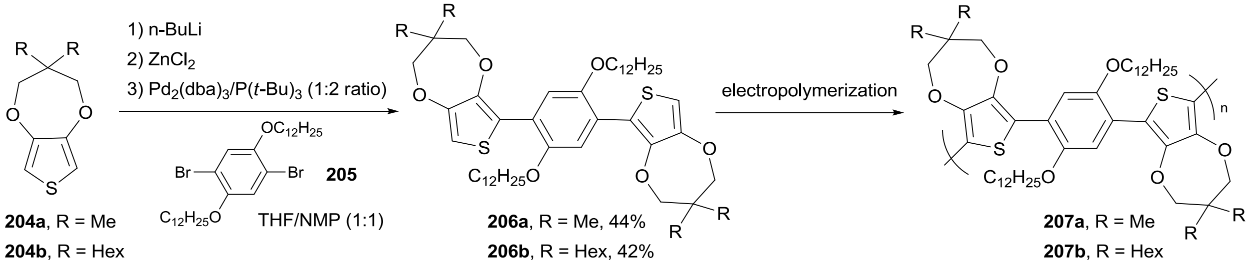
Scheme 53. Synthesis of heterodimetallic Ru-Os complex **201**.

Ren and co-workers demonstrate that the Negishi coupling is a facile, mild, and high-yield approach, superior to the Suzuki method, for biphenyl formation at the periphery of diruthenium coordination and organometallic compounds.[145] As shown in **Scheme 54**, coordination compounds **202a-c** and organometallic compounds **203a-c** were prepared in 75-92% yields (47% for **203a**) by using the Negishi coupling, and reactions proceed at room temperature.[145a] In contrast, **202a** was previously prepared using the Suzuki coupling only in 41% yield.[145b]



Scheme 54. Synthesis of **202** and **203**.

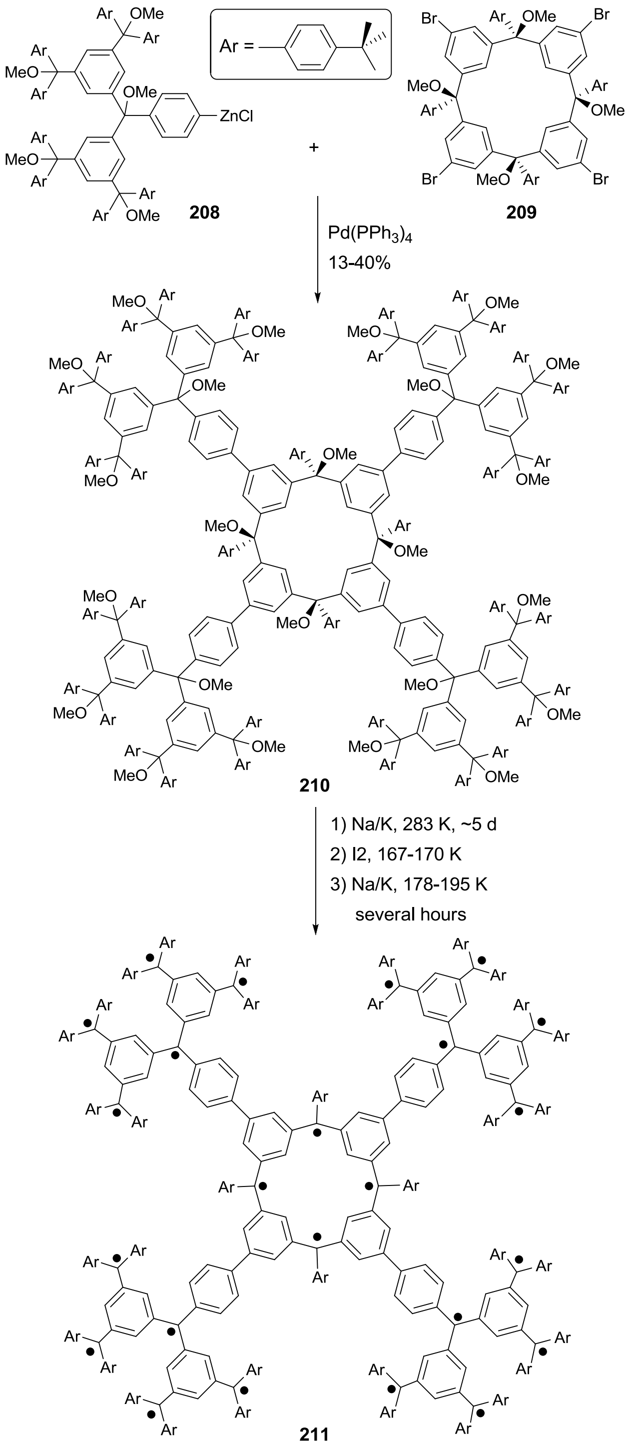
The monomers 1,4-bis[2-(3,3-dimethyl-(3,4-propylenedioxy)thienyl]-2,5-didodecyloxybenzene (**206a**) and 1,4-bis[2-(3,3-dihexyl-(3,4-propylenedioxy)thienyl]-2,5-didodecyloxybenzene (**206b**) were synthesized via Negishi coupling of the alkyl-substituted ProDOT **204a** and **204b** and didodecyloxyphenylene unit **205** in ca. 40% yields (**Scheme 55**).[146] Both the monomers were efficiently electropolymerized to form electroactive films exhibiting redox switching at fairly low potentials (ca. +0.1 V vs Fc/Fc+). Polymer **207b** electrochemically switches between orange, blue, and highly transmissive-gray colors, making it potentially useful in large area electrochromic displays.



Scheme 55. Synthesis of **207a** and **207b**.

5. Magnetic materials and high spin organic polyradicals

Organic molecules with a very high spin possess a large number of ferromagnetically coupled unpaired electrons (parallel spins), and such paramagnetic organic polyradicals are not only the building blocks for organic magnets[147] but may also exhibit other interesting electronic, optical, and electrochemical properties.[148] To achieve a high spin quantum number *S* (high-spin ground state) becomes a major task for the researchers in this field. A unique dendritic macrocyclic organic spin cluster **211** with a very high spin of S=10 has been synthesized.[149] The synthesis of the precursor **210** relies on the attachment of four dendritic branches to the macrocyclic core by the four-fold Negishi coupling of the zincated pentaether **208**, generated in situ from the corresponding bromopentaether by the bromine-lithium exchange using ^{t}BuLi followed by the treatment with ZnCl$_2$, with macrocyclic tetrabromide **209** (**Scheme 56**). Yields ranging from 10-40% were reported for this highly demanding synthesis.



Scheme 56. Synthesis of organic spin cluster **211**.

The Negishi protocol was further employed in a macrocycle-macrocycle coupling to make a series of marcocycle assemblies by linking two to five calix[4]arene-based polyarylmethyl polyether macrocycles.[150] Polyarylmethyl polyradicals derived from those assemblies display very high spin S = 5-13. Remarkably, polyarylmethyl polyradical **214** (**Figure 2**) has the highest spin quantum number of S = 13 for an organic molecule reported so far. The precursor to the high spin macrocycle assembly **214** was prepared by four-fold Negishi coupling of tetrazincated tetraether macrocycle **212** (from **209**) with monobrominated polyether macrocycle **213** in 7-32% yields under the same conditions described in **Scheme 56**.

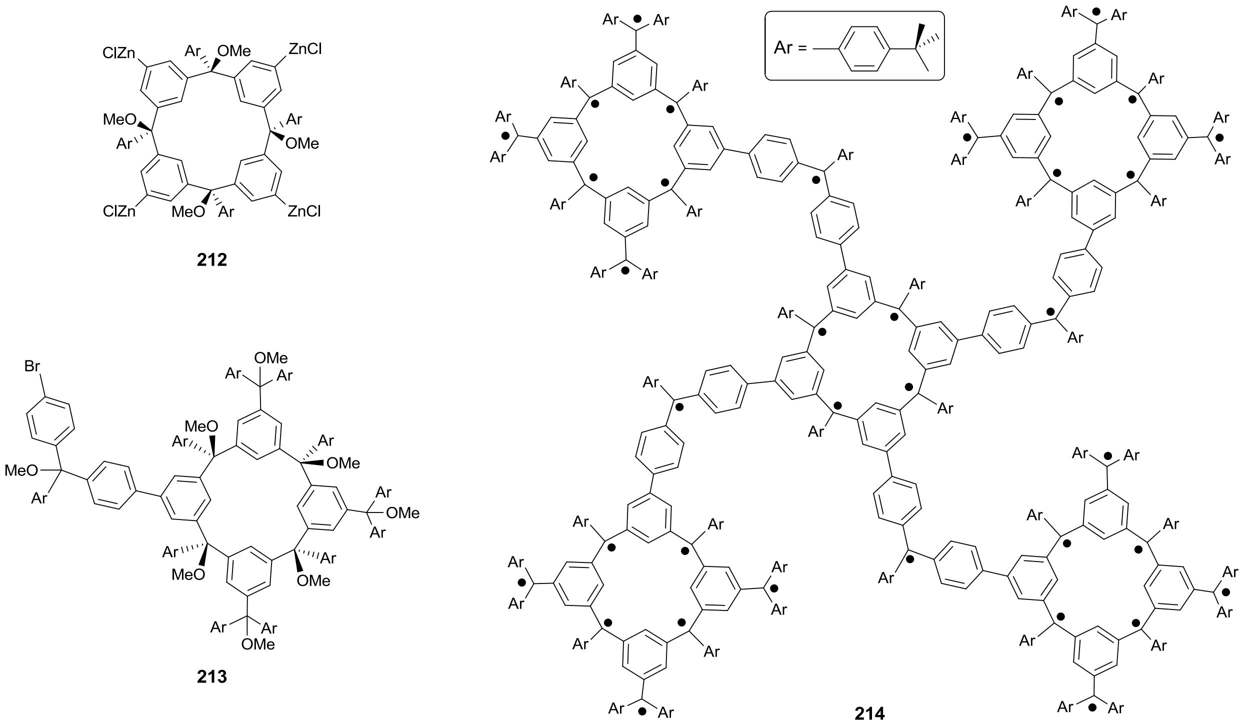
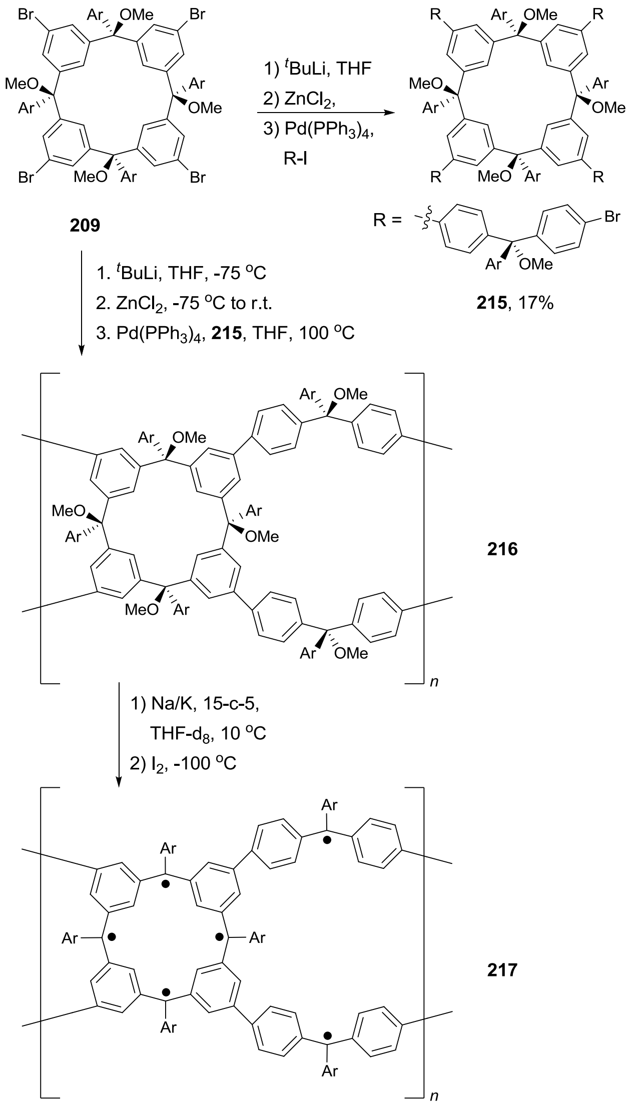


Figure 2. Structure of high spin polyarylmethyl polyradical macrocycle assembly **210**.

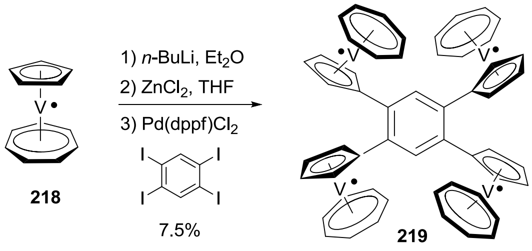
Polymers with high spin quantum number (S) were very much limited to $S<5$ until Rajca's novel design and synthesis of polymer networks with cross-linked macrocyclic modules possessing an average of $S \geq 40$.[151] The cross-linking was realized by the Negishi coupling as shown in **Scheme 57**. First, tetrabromide **209** was converted to a new tetrabromide **215** via a one-pot lithium-bromine exchange/zincation/four-fold cross coupling process. In the second step, **209** was again converted to its zincated derivative (**212**) and cross coupled with the tetrabromide **215** in the presence of catalyst $Pd(PPh_3)_4$ to give the cross-linked polymer **216**, the precursor to **217**. In a later study, the highly cross-linked polymer is produced using the same synthetic strategy, and displays an effective magnetic moment corresponding to an average S of about 5,000 and slow reorientation of the magnetization by a small magnetic field (less than or equal to 1 oersted) below a temperature of about 10 K.[152] The magnetic behavior falls between insulating spin glasses and blocked super-paramagnets.



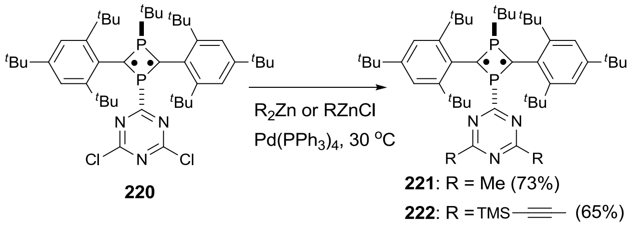
Scheme 57. Synthesis of cross-linked magnetic polymer **217**.

Tetra- and octaradicals based on calix[4]arene nitroxides were prepared recently by Rajca and co-workers, and the Negishi coupling was once again used to introduce nitroxide fragments to the calix[4]arene core.[153] Elschenbroich and co-workers reported an organometallic tetraradical displaying pronounced electro- and magnetocommunication. The organometallic tetraradical **219** was prepared via four-fold Negishi coupling of $(C_7H_7)V(C_5H_4ZnCl)$ (**218**) with 1,2,4,5-tetraiodobenzene (**Scheme 58**).[154] More recently, the Negishi coupling was applied to the modification of a triazine-substituted biradical

220 to obtain more stable derivatives **221** and **222** (**Scheme 59**).[155] The Sonogashira coupling conditions were not suitable for preparing **222** because of an undesirable Hoffmann reaction with the amine.



Scheme 58. Synthesis of tetraradical **219**.



Scheme 59. Negishi coupling of biradical **220**.

6. Conclusions and perspectives

The Negishi coupling has played an important role in the development of advanced organic materials, allowing the synthesis of a wide variety of molecules exhibiting different functions including electronic conducting, light-emitting and other optical functions, redox activities, and magnetic properties. Many of the syntheses are very challenging but could be tackled with the Negishi coupling. For example, reactions involving multifold Negishi cross couplings often give satisfactory results that cannot be achieved by using other methods. The Negishi coupling is also extremely efficient in introducing an aromatic or heteroaromatic unit because many of the aromatic/heteroaromatic zinc reagents can be generated in situ from inexpensive starting materials and used directly in the cross coupling. More importantly, the reaction usually proceeds under mild conditions and gives a high yield of the desired product, and in most cases, palladium catalysts with simple triphenylphosphine ligands can serve the purpose of the synthesis. Although polycondensation using the Suzuki coupling predominates the synthesis of conducting polymers, a recent study demonstrates that the Negishi polycondensation can have several clear advantages such as lower catalyst loading (higher TONs) and faster reaction rate (higher TOFs).[49] Moisture and oxygen-free conditions seem to be the limitation of the Negishi coupling compared to the Suzuki coupling, however, such conditions, in many cases, are beneficial to the synthesis itself in terms of the efficacy of reaction, for example, producing high-quality polymers and increasing the lifetime of the catalyst. As more of its unique merits are discovered, we believe that the Negishi coupling will gain increasing popularity in organic synthesis. Advanced technologies based organic electronic, optical, electrochemical, and magnetic materials can have profound influence on improving the quality of human life while, in the meantime, address associated global issues such as energy crisis and environmental conservation. The Negishi coupling will continue to make its unique contribution to the development of new materials with multiple functions to improve these technologies.

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