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Synthesis, structure control and functions of polymers containing conjugated transition metal complex moieties

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Polymers containing conjugated platinum (Pt) complex moieties in the main/side chains are potential high-performance materials that combine the catalytic and photoelectric functions of Pt complexes with the photoelectric properties and formability of π-conjugated polymers. The present article overviews the synthesis of Pt-containing polymers using a variety of polymerization methods, including dehydrochlorination coupling polymerization of PtL_2Cl_2 (L: ligand) with $HC{\equiv}C{-}Ar{-}C{\equiv}CH$ (Ar: arylene) and ring-opening metathesis polymerization of norbornene monomers bearing Pt complex moieties. In addition, structural control by intra/intermolecular Pt–Pt, Pt–π, π–π, hydrogen bonding and van der Waals interactions is described. Finally, the review describes the development of applications of these materials, including catalysis for hydrosilylation and oxidation of alkenes, as well as photon upconversion, circularly polarized luminescence, mechanochromism and chiral recognition.

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1. Introduction

Remarkable progress has been made in the chemistry of transition metal complexes in the past half century, especially considering the much longer history of the main-group elements. Transition metal complexes have been widely utilized in industrial applications as well as academic fields because they exhibit a variety of reactivities and catalytic activities not found in typical elements. Ferrocene was one of the earliest well-defined transition metal complexes, first synthesized in 1951,[1] and the precise structure was determined in 1952.[2] Since ferrocene features reversible redox properties and easy functionalization, it has been variously employed as a component of functional materials. For example, poly(vinylferrocene), which is synthesized by radical polymerization of vinylferrocene, exhibits redox properties, including electrochemical oxidation,[3] switchable surface wettability,[4] redox-response of block copolymers with poly(lactide),[5] dispersion and redox-controlled precipitation of carbon nanotubes,[6] electrochemical selective formate separation,[7] and enhancement of ionic conductivity of lithium–sulfur batteries.[8]

Inspired by poly(vinylferrocene), various metal-containing polymers have been synthesized, such as poly(meth)acrylate, poly(styrene) and poly(norbornene) derivatives bearing metal-complex moieties in the side chains,[9] aiming at application in biomedical materials such as drug delivery vehicles, antimicrobial and antiviral agents, and biosensors and in bioimaging.[10] The other research studies on metal-containing polymers include polymers mainly containing iron in the main chain;[11] metallosupramolecular polymers containing bipyridine and terpyridine ruthenium and some other transition metal complexes;[12] preparation and applications of double-helical copper-based polymers in sensors, catalysis and optoelectronics;[13] photo-responsive polymers containing ruthenium complex and heteroatom moieties, enabling sensitive and selective photochemical responses;[14] controlled polymerization reactions including atom transfer radical polymerization and reversible addition–fragmentation chain-transfer polymerization for preparing metallopolymers;[15] and metallopolymers exhibiting tunable electrical, magnetic and optical properties, which are applicable in memory devices, stimuli-responsive materials, luminescence, self-healing, supercapacitors and biomedicine.[16]

Biological proteins exhibit sophisticated functions at ambient temperature and pressure in order to regulate biological phenomena. The functions of metalloproteins of course depend on the primary structure, and they also largely depend on hierarchical higher-order structures, *i.e.*, secondary structure, α-helix and β-sheet; tertiary structure, the three-dimensional arrangement of the polypeptide chain in space; and quaternary structure, the assembly of multiple polypeptides. Thus, the synthesis of artificial metal-containing polymers with controlled higher-order structures is highly desired for the development of materials that, like metalloproteins, exhibit sophisticated functions.

π-Conjugated polymers, such as poly(acetylene) and poly(phenylene), exhibit photo-electronic properties, and are applicable to light-emitting materials, solar cells, electrodes and antistatic materials.[17,18] π-Conjugated polymers are conformationally less mobile than non-π-conjugated polymers because the main chains consist of sp^2- and/or sp-hybridized carbons, while those of non-π-conjugated polymers contain sp^3-hybridized atoms. As a result, π-conjugated polymers tend to form higher-order structures like helices, twisted ribbons, foldamers, assemblies and aggregates. π-Interaction also contributes to induction of higher-order structures of π-conjugated polymers. The incorporation of transition metal complex moieties into π-conjugated polymers possibly leads to highly sophisticated functional polymeric materials that integrate both transition metal complexes and π-conjugated polymers synergistically, including catalysis, photoelectric function, higher-order structure formation, stimulus response and formability. It is also notable that the fusion of transition metal complexes and π-conjugated polymers remarkably enhances the diversity of molecular design, leading to a wide variety of polymers compared with polymers consisting only of main-group elements.

Thus far, various reviews concerning the synthesis and properties of metal-containing polymers have been reported as described above. However, these reviews do not focus on the control of higher-order structures of metal-containing polymers. The present article overviews the synthesis and structural control of coordination polymers containing conjugated transition metal complex moieties, primarily Pt complexes (Fig. 1), and their applications including catalysis, photon upconversion, circularly polarized luminescence (CPL), mechanochromism and chiral recognition (Fig. 2).

2. Synthesis of polymers containing conjugated Pt complex moieties

2.1 Synthesis and control of conjugation of Pt complex-containing polyaryleneethynylene

Pt has a silvery-white metallic luster and is widely used in jewelry due to its high scarcity value, as well as its high resistance to heat, discoloration and corrosion. Pt is also widely used in industrial fields because of the high catalytic activity for hydrogenation and hydrosilylation of olefins, as well as detoxification of gas exhaust from automobiles. π-Conjugated polymers containing Pt complex moieties in the main/side chains are expected to be high-performance materials that combine the catalytic and photoelectric functions of Pt com-

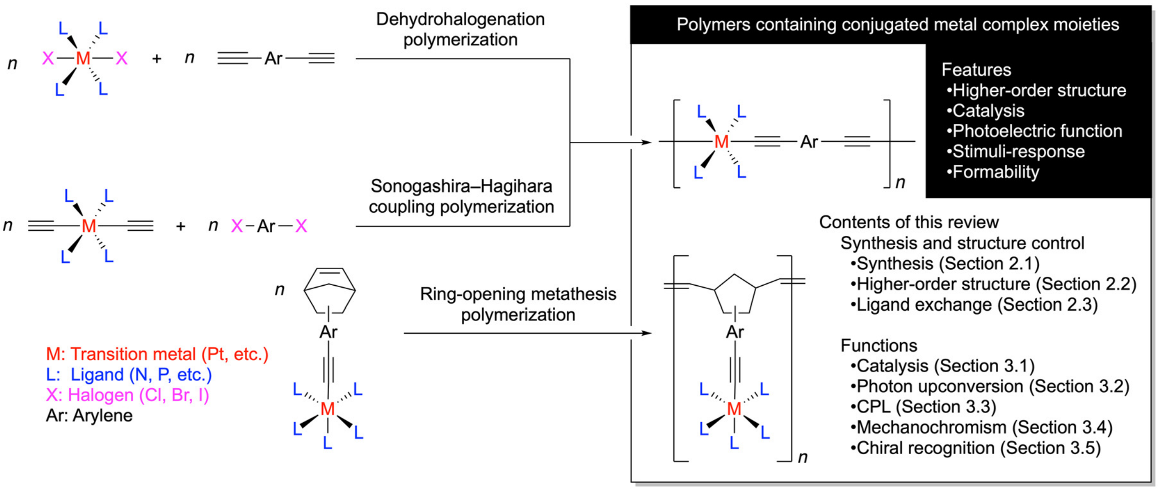


Fig. 1 Synthesis and features of polymers containing conjugated metal complex moieties.

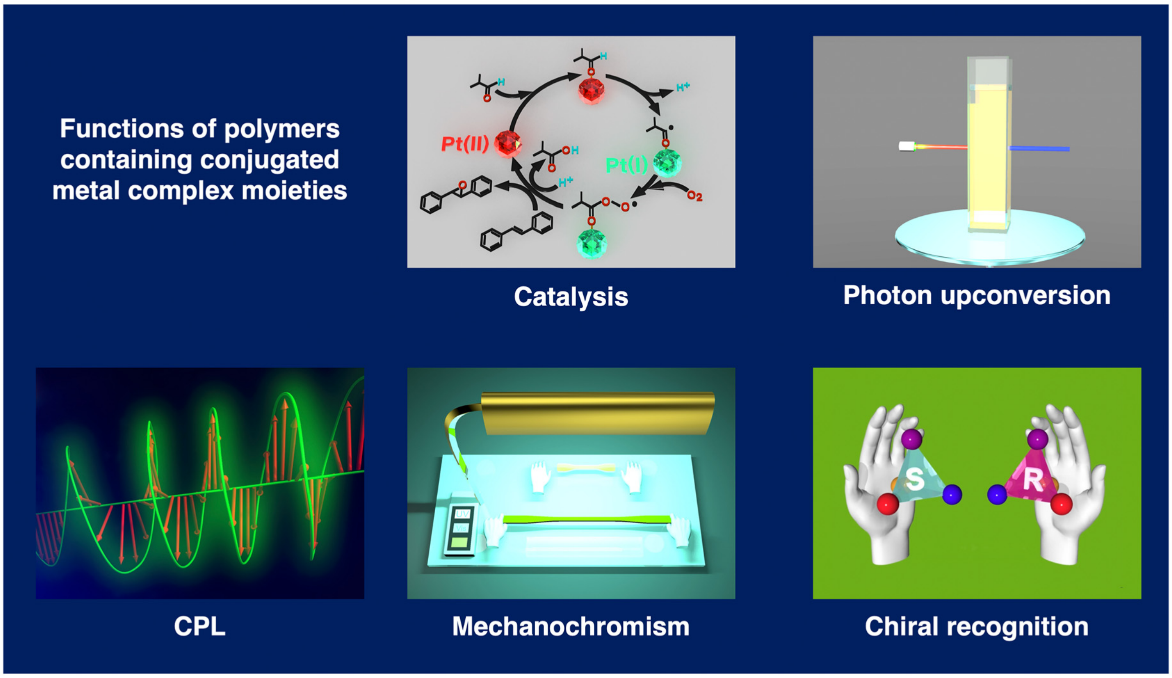


Fig. 2 Functions of polymers containing conjugated metal complex moieties.

plexes with the photoelectric properties and formability of π-conjugated polymers.

Pt-acetylide polymers, first reported in 1975,[19] are synthesized by copper iodide (CuI)-catalyzed dehydrochlorination of $Pt(PR_3)_2Cl_2$ complexes with diethynylarylenes in the presence of an amine (Fig. 3). Pt-acetylide polymers are resistant to moisture and are stable in air, and they exhibit liquid crystalline properties owing to the rigid backbone.[20] Pt-acetylide polymers are finding applications in electronic and optical devices, chemical sensors and patternable precursors of magnetic metal alloy nanoparticles.[21] The analogous metal acetylide polymers, *trans*-$[-M(PR_3)_2-C{\equiv}C-Ar-C{\equiv}C-]_n$ (M = group 8–10 transition metals), have also been synthesized by the Stille coupling reaction of $Pt(PR_3)_2Cl_2$ with $Me_3Sn-C{\equiv}C-Ar-C{\equiv}C-SnMe_3$,[22–24] but those polymers were less stable compared with Pt-acetylide polymers.

One interesting application of Pt-acetylide complexes is their usage as building blocks of "dendrimers", macromolecules with a regularly branched three-dimensional structure. The first dendrimer was synthesized in a cascading manner, using an iterative sequence of reaction steps.[25] The synthetic methods for dendrimers are categorized as either "divergent methods" or "convergent methods" (Fig. 4). Using the divergent method, dendrimers are synthesized in a stepwise manner from a central core to the outer shell. Using the convergent method, "dendrons" are synthesized as the surface of the dendrimer sphere beforehand, and are connected to a core molecule to obtain dendrimers. Dendrimers gather attention as polymeric materials featuring properties different from those of common linear polymers with the same monomer units.[26]

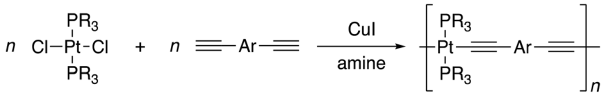


Fig. 3 Synthesis of the Pt-acetylide polymer.

There are various reports on "metallodendrimers", dendrimers containing organometallic complex moieties in the main or side chain, surface or core. Various metallodendrimers tethering metal complex peripherals have been synthesized and their functions have been investigated. For example, siloxane polymers,[27] silane[28,29] and amide/urea[30] dendrimers bearing arylnickel(II) complex moieties regiospecifically catalyze the Kharasch addition of polyhalogenoalkanes to carbon–carbon double bonds. In addition, carbo-silane dendrimers with $(\eta^3\text{-}C_4H_7)Pd$ complex moieties catalyze hydrovinylation of styrene, enabling continuous reaction using a nanofiltration membrane.[31]

A benzenetricarboxylate-cored dendrimer tethering a Pt-pincer complex peripheral selectively adsorbs SO_2 gas to change the color significantly.[32,33] Dendrimers with tetrahedral Cu(I) cores and Schiff-base-derived polycatenary ligands exhibit liquid crystalline properties.[34] A series of linear polymers and benzene-cored dendrimers containing Pt/Pd acetylide[35,36] and Ru acetylide[37] complex moieties have been synthesized (Fig. 5), including giant sixth-generation Pt-acetylide dendrimers with diameters larger than 10 nm bearing as many as 189 Pt atoms per molecule.[38] Porphyrin-cored dendri-

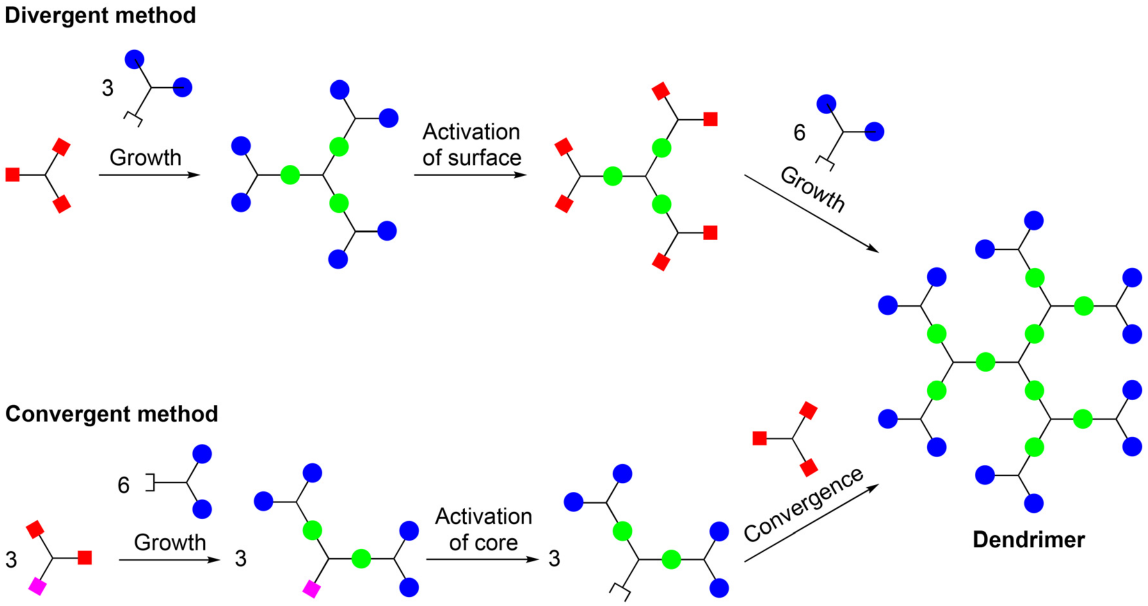


Fig. 4 Divergent and convergent methods for synthesizing a dendrimer.

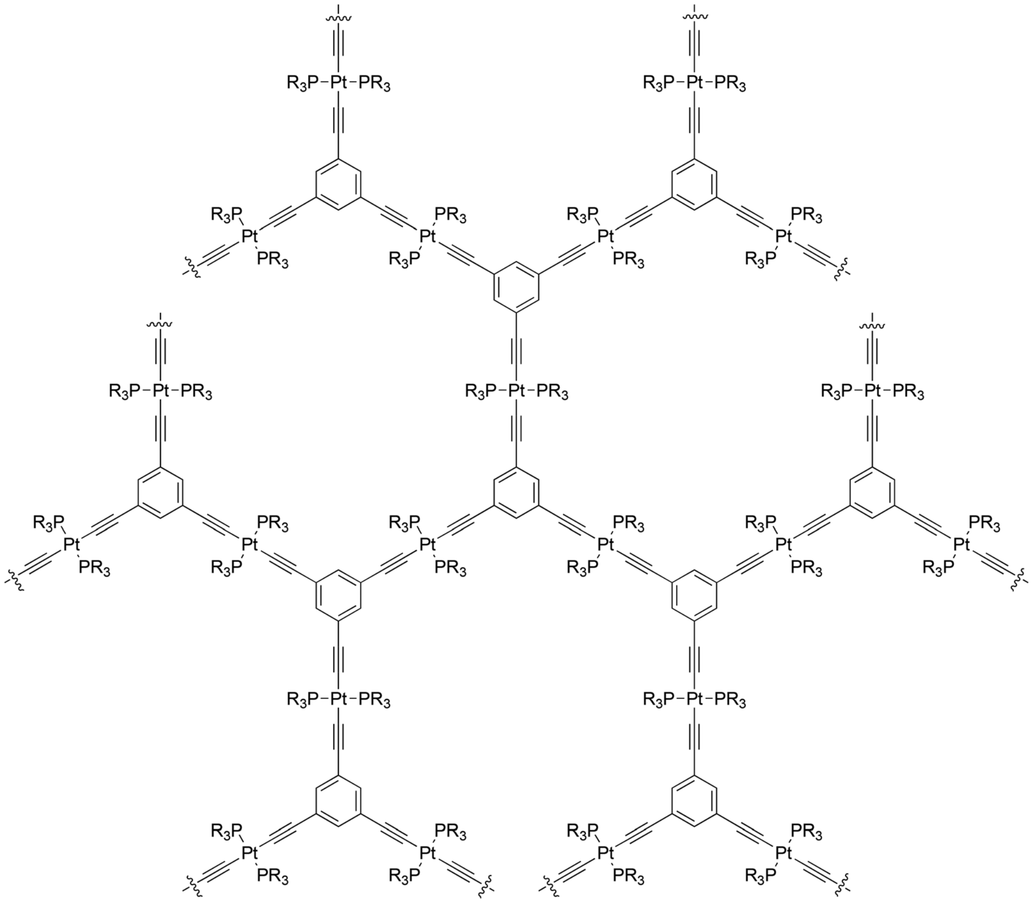


Fig. 5 Representative structure of a Pt-acetylide dendrimer synthesized by the convergent method.

mers containing Pt-acetylide complex moieties exhibit decreased fluorescence with increasing dendrimer generation.[39] A dendrimer with $-Pt(PEt_3)_2-C{\equiv}C-Pd(PEt_3)_2-Cl$ units serves as a multifunctional initiator for living polymerization of isocyanides to give dendrimers bearing poly(isocyanide) arms with controlled molecular weights and dispersities.[40] Polymers[41] and dendrimers[42] with C_2-symmetric (*R*)-binaphthol linkages show large optical rotations (*e.g.*, $|[\alpha]_D| = 370°$). Okamura *et al.* incorporated L-amino acid moieties in the backbones of Pt-acetylide complex-containing polymers to induce large optical activities.[43,44] These polymers are applicable to the construction of cavities or binding sites of artificial enzymes.

Phosphine ligands such as triphenylphosphine and tributylphosphine are widely employed for Pt-acetylide polymers as described above. Nitrogen ligands such as ammonia, amines, pyridine, bipyridine and terpyridine derivatives are also employed in a manner similar to that observed in other Pt complexes. *N*-heterocyclic carbene (NHC) has strong coordination ability that exceeds that of phosphine and nitrogen ligands. NHC-coordinated transition metal complexes are stable and exhibit catalysis for hydrosilylation of alkenes, alkynes and ketones, hydrogenation of alkenes, Heck olefination, hydroformylation and olefin metathesis reactions.[45] π-Conjugated aromatics-containing NHC complexes of transition metals, including rhenium, ruthenium (Ru), osmium, rhodium, iridium, nickel, palladium (Pd) and Pt, are highly luminescent based on metal-to-ligand charge transfer (MLCT). They are applicable in photocatalytic water-splitting catalysts, chemosensors, dye-sensitized solar cells, oxygen sensors and medical scenarios.[46] A series of NHC ligand-containing Pt-acetylide complexes have been synthesized (Fig. 6), including *trans*-$(NHC)_2Pt(C{\equiv}C-Ar)_2$,[47,48] $(NHC)_2Pt(C{\equiv}C-C{\equiv}C-R)_2$[49] and $-[-(NHC)_2PtC{\equiv}C-Ar-C{\equiv}C-]_n-$,[50] to confirm that NHC ligands significantly enhance the phosphorescence quantum yields compared to phosphine ligands. Organic light-emitting diodes (OLEDs) using NHC ligands as emitters exhibit electroluminescence. Additional device engineering is expected to further improve the performance of OLEDs.

A series of *meta*- and *para*-phenylene-linked poly(aryleneethynylene)s bearing Pt in the main chain have been synthesized by the Sonogashira–Hagihara coupling polymerization of bis[(ethynylphenyl)ethynyl]bis(butylphosphine)Pt monomers with dibromoarylene monomers using Pd and Cu catalysts (Fig. 7) to investigate the relationship between their optical and aggregation properties.[51] The maximum absorption wavelengths of the *meta*-phenylene-linked polymers are shorter than those of the *para*-phenylene-linked counterparts. Apparently, the conjugation length of the *meta*-phenylene-linked polymers is shorter than that of their corresponding *para*-phenylene-linked counterparts. The wavelengths of maximum absorption and emission of the *meta*- and *para*-phenylene-linked polymers increase in the order: Ar = 1,4-phenylene < 1,4-naphthalene < 9,10-anthracene, in agreement with the order of maximum absorption wavelengths of the corresponding aromatics: benzene (255 nm) < naphthalene (286 nm) < anthracene (375 nm). The number of fused aromatic rings apparently affects the absorption and emission properties of the polymers.

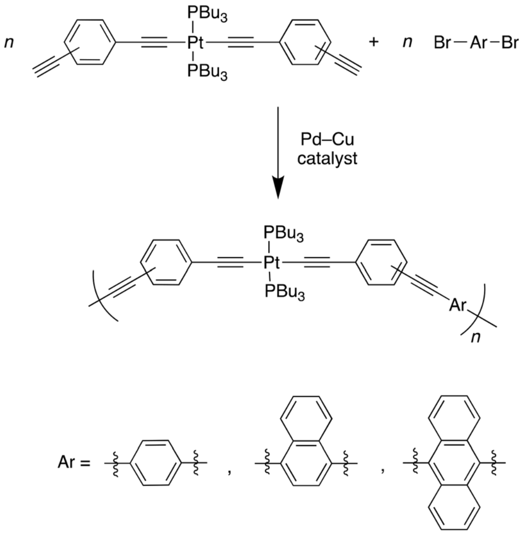


Fig. 7 Synthesis of poly(aryleneethynylene)s bearing Pt in the main chain by Sonogashira–Hagihara coupling polymerization.

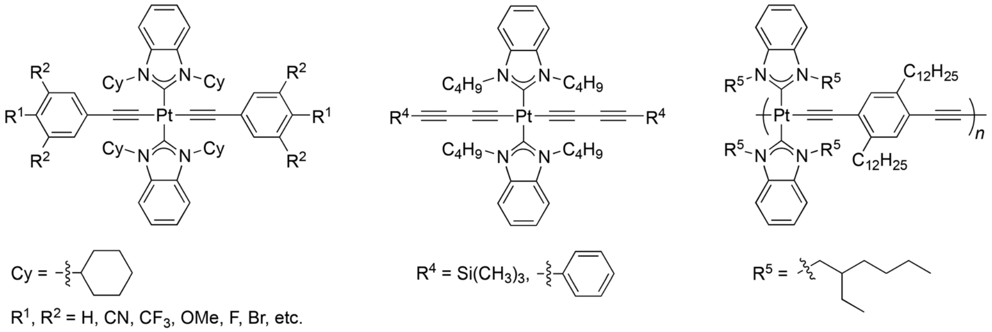


Fig. 6 NHC ligand-containing Pt-acetylide complexes.

2.2 Control of higher-order structures of Pt complex-containing polyaryleneethynylenes

A series of hierarchically self-assembled cyclic metal complexes have been reported, in which molecular units were assembled into ordered secondary structures through non-covalent interactions.[52] They serve as building blocks for more complex multi-functional supramolecular structures. The hierarchical self-assembling strategy was used as a versatile method for preparing size- and shape-defined nanostructures. They are constructed based on metal–ligand coordination, hydrogen bonding, π–π and van der Waals interactions, which are controllable and tunable by temperature, solvent, pH, *etc*. This concept is also applicable to induce higher-order structures in polymers containing metal complex moieties.

Poly(phenyleneethynylene)s substituted with optically active groups form chiral higher-order structures, predominantly one-handed helices and/or chiral aggregates, due to the small mobility of the conjugated main chains and solvophobic effects.[53] The higher-order structures are also stabilized by intra- and/or intermolecular noncovalent interactions such as π-stacking, hydrogen bonding and van der Waals interactions.[54] The chiral higher-order structures and optical properties of D-hydroxyphenylglycine-derived polymers containing Pt in the main chain have been investigated (Fig. 8).[55] The polymers exhibit negligibly small CD signals in THF, while intense CD signals are observed in the absorption region of the main chain chromophore around 320–420 nm in THF/MeOH = 1/9. The UV–vis absorbance is small in THF/MeOH = 1/9 compared with that in THF. In THF/toluene, the CD intensity gradually increases with increasing toluene content, accompanied by a small decrease of the UV–vis absorbance.

Poly(*meta*-phenyleneethynylene)s form aggregates or foldamers under certain conditions.[56] The $\lambda_{\max}$ of the UV–vis absorbance of poly(phenyleneethynylene)s commonly depends on the conformation, random coil and helix,[57] while no remarkable difference of the $\lambda_{\max}$ values of the Pt-containing D-hydroxyphenylglycine-derived polymers between helically folded and aggregated forms was observed. One possible reason is the presence of amide groups, which suppress the molecular mobility of the polymers by forming inter/intramolecular hydrogen bonding, resulting in almost the same $\lambda_{\max}$ values irrespective of the presence of helically folded and aggregated forms. Particles with hydrodynamic diameters around 100 nm were detected in a polymer solution of THF/MeOH = 1/9, while no particles were detected in a polymer solution of THF/toluene = 1/9. These results indicate that the polymer formed chiral aggregates in THF/MeOH = 1/9 and a predominantly one-handed helix in THF/toluene = 1/9.

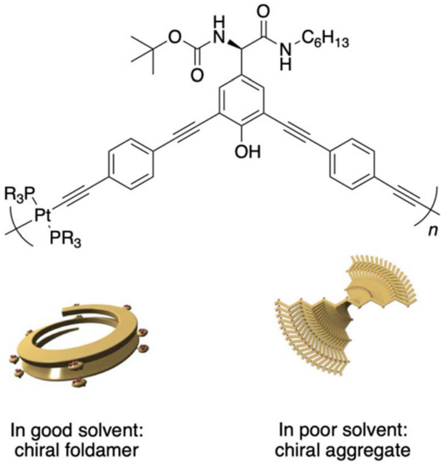


Fig. 8 Solvent-dependent higher-order structures of D-hydroxyphenyl glycine-derived Pt-containing poly(phenyleneethynylene).

These results indicate that poly(aryleneethynylene)s containing Pt complex moieties in the main chain form higher-order structures due to their rigidities, which are controllable by the environment. Furthermore, various optically active amide groups capable of hydrogen bonding and π-interaction have been introduced into ligands, and the steric coordination and higher-order structures of the polymers were successfully controlled by ligand–ligand interactions.[58,59]

The catalytic activity and selectivity of phosphine-ligated transition metal complexes are tunable according to the electronic and steric characteristics of the phosphine ligands, as well as the metal species and valence. Introduction of chirality in the phosphine ligands has been actively examined in order to develop transition metal catalysts for asymmetric induction. In addition, transition metal complexes with amino-acid- and peptide-functionalized phosphine ligands adopt well-defined conformations stabilized by intramolecular hydrogen bonding between the peptides (Fig. 9), and they catalyze asymmetric reactions such as hydrogenation.[60–62] An artificial pseudo C_2-symmetric peptide turn is formed to control the chirality of the coordination sphere of the prochiral catalytic metal. The amino acid substituents strongly affect the selectivity of the catalytic reaction, indicating that chirality transfer is an important tool in asymmetric catalysis. This approach allows for flexible design of the coordination sphere of catalytic metals and opens a new means of catalytic design.

Pt-containing conjugated polymers have been synthesized by the dehydrochlorination coupling polymerization of *cis*- and *trans*-PtL_2Cl_2 {L = $P(Ph)_2$-*p*-$C_6H_4CONHCH[CH(CH_3)_2]CO_2CH_3$} with 1,4-diethynylbenzene, in order to obtain poly-

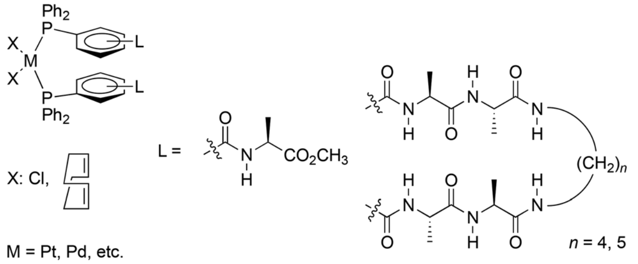


Fig. 9 Metal complexes with amino-acid- and peptide-functionalized phosphine ligands.

mers with controlled geometry at the Pt centers (Fig. 10).[58] In the polymerization of *cis*-PtL_2Cl_2, the geometry at the Pt centers is controlled by the amine used in the polymerization and the reaction temperature. The polymer with *trans*-Pt centers exhibits a CD signal in the main chain chromophore region in a CH_2Cl_2/MeOH mixed solvent. Based on the crystal packing state and non-covalent interaction analysis of a model compound, the chiroptical activity is attributed to aggregation stabilized by intermolecular π–π, CH–π, and hydrogen-bonding interactions between the phosphine ligands.

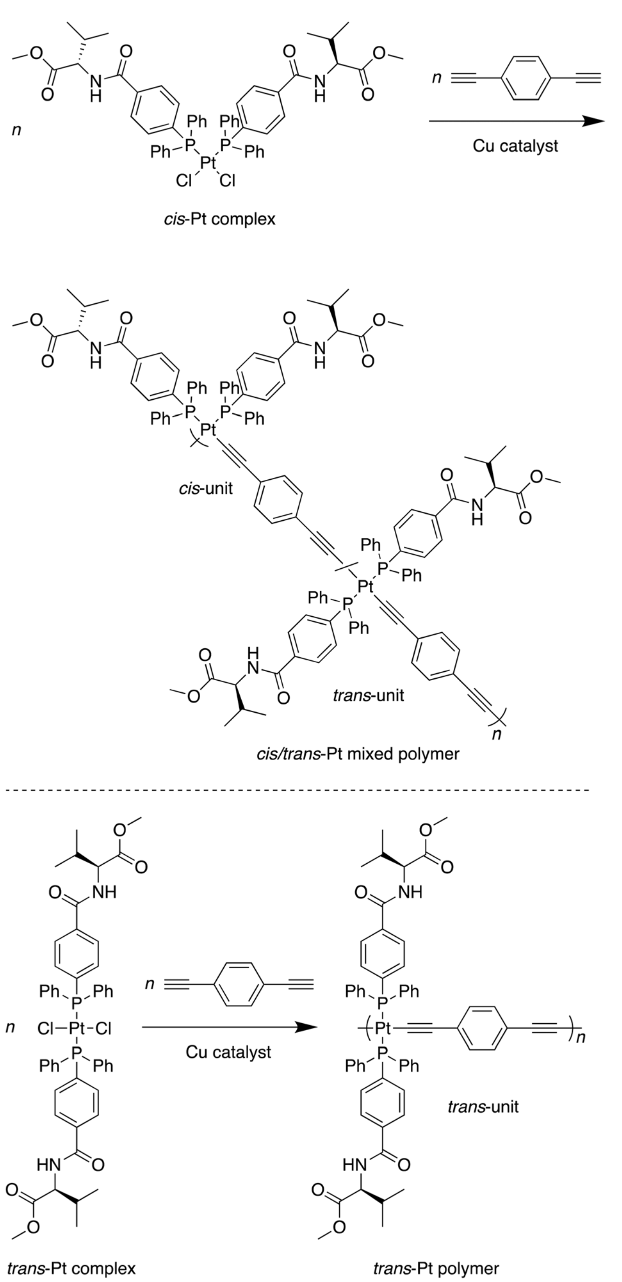


Fig. 10 Polymerization of *cis*- and *trans*-Pt complexes with 1,4-diethynylbenzene.

A series of poly(phenyleneethynylene)s containing Pt complexes with various phosphine ligands have been synthesized to examine the effect of phosphine substituents on the main chain conjugation (Fig. 11).[63] The maximum absorption wavelength depends on the degree of resonance stabilization of the phosphine ligands and was confirmed by quantum chemical calculations. This result indicates the dependence of main-chain conjugation of Pt-containing conjugated polymers on the phosphine ligands in the side chains. Thus, the conjugation of the polymers can be controlled by ligand selection of Pt complexes without changing the structures of the main chains.

2.3 Induction of asymmetric higher-order structures by ligand exchange

Reactive polymers are useful precursors of a wide variety of functional polymers. The introduction of reactive groups remarkably broadens the molecular design possibilities, including the formation of block copolymers by inserting various segments. The reactions of metal complex moieties in conjugated organometallic polymers are particularly promising for preparing novel metal-containing polymers that cannot be prepared directly.[64] $(PPh_3)_2PtL_2$ complexes undergo ligand exchange reactions of PPh_3 with PR_3 (R = alkyl) because the coordination ability of PPh_3 is smaller than that of PR_3. $(PPh_3)_2PtL_2$ complexes also undergo exchange of PPh_3 with diphosphines to form stable chelated Pt complexes.[65–67] Both *cis*- and *trans*-configurations are possible at the metal centers of Pt-acetylide complexes. Employment of a diphosphine ligand, $Ph_2P–(CH_2)_2–PPh_2$ leads to a *cis*-Pt-configuration due to geometrical restrictions,[68] but Pt-acetylide polymers with monophosphine ligands are likely to adopt a *trans*-configuration due to thermodynamic favorability. Even if the configuration of the precursor (PtL_2Cl_2, L = ligand) is *cis*, Pt-acetylide polymers transform into the *trans*-configuration by isomeriza-

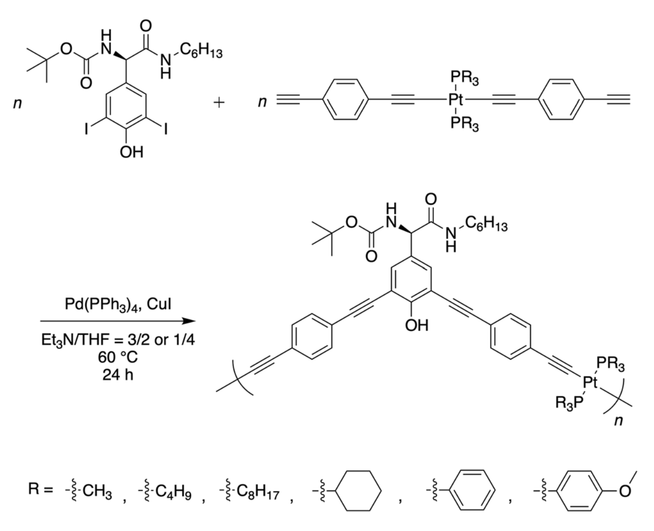


Fig. 11 Synthesis of optically active poly(phenyleneethynylene)s bearing various phosphine ligands.

tion during the dehydrochlorination process. Ligand exchange reactions are also applicable in the control of double helical structures of Pt-containing dimers.[69] Since *cis*/*trans*-geometries and the ligand structure remarkably affect the photoelectric properties and shapes of Pt-acetylide polymers, control of the conformation and properties can be achieved by utilizing the ligand exchange reaction. Pt-containing optically active polymers have been synthesized by ligand exchange of a $Pt(PPh_3)_2$-containing polymer (Fig. 12),[70] and the conformation was investigated. The geometry of the Pt center is *trans*, as confirmed by ^{31}P NMR spectroscopy. After ligand exchange, the geometry of the Pt center converted to *cis*. On the other hand, the geometry at the Pt center of the $Pt[Ph_2P(CH_2)_3PPh_2]$-containing polymer remained *trans*.

Fig. 13 shows the possible structures of Pt-containing polymers having *trans* Pt centers bridged with $Ph_2P(CH_2)_mPPh_2$ (m = 2 and 3) ligands. One $Ph_2P(CH_2)_2PPh_2$ molecule coordinates to one Pt atom with a *cis* configuration. On the other hand, one $Ph_2P(CH_2)_3PPh_2$ molecule coordinates to two Pt atoms at the ith and (i + 6)th units with a *trans* configuration. This result was supported by molecular modeling, as shown in Fig. 14.

As described above, the ligand exchange reaction of optically active polymers with optically inactive phosphine ligands successfully gives polymers with controlled secondary structures. The ligand exchange reaction of optically inactive polymers with optically active phosphine ligands also gives structure-controlled polymers. As shown in Fig. 15,[71] an intramolecular bridging reaction gave a predominantly one-handed folded helical polymer exhibiting intense CD signals based on exciton coupling. The conformation was supported by the TD-DFT-simulated CD spectrum. This methodology provides a new means to control inter/intramolecular crosslinking/bridging in the side chains of polymers, as well as induction of chirality in optically inactive metal-containing polymers by utilizing optically active ligands.

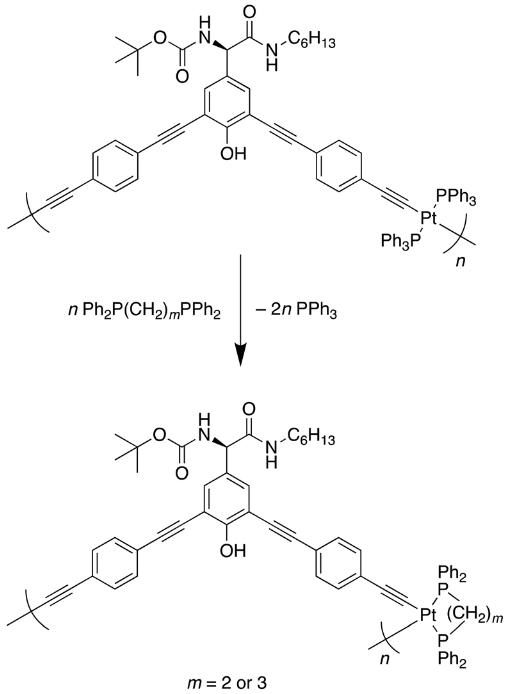


Fig. 12 Ligand exchange reaction of a $Pt(PPh_3)_2$-containing polymer with $Ph_2P(CH_2)_mPPh_2$ (m = 2 or 3).

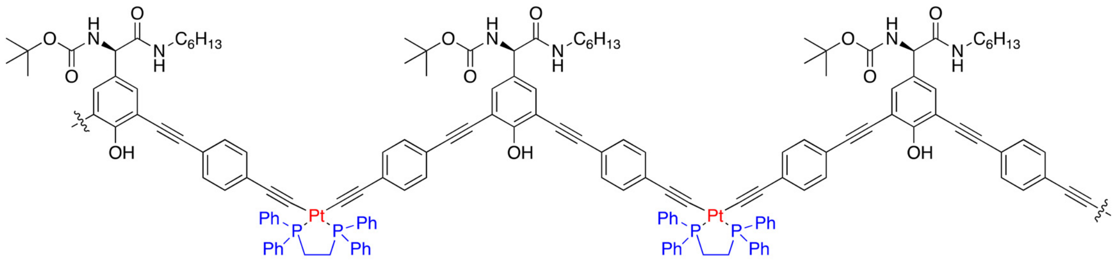
Other types of optically active phosphine ligands that have P-chirality include 1,2-bis(*tert*-butylmethylphosphino)benzene (BenzP*) and 2,3-bis(*tert*-butylmethylphosphino)quinoxaline (QuinoxP*).[72] BenzP* and QinoxP* are air-stable, especially QuinoxP*, and applicable as ligands for transition metal complexes that catalyze enantio-selective hydrogenation,[73,74] aldol reaction[75] and borylation.[76] QuinoxP* is also usable as a building block of Pt-containing polymers, in which QuinoxP* plays a significant role in chirality induction to the polymer main chain.[77] BenzP* and QuinoxP* have been employed as chiral phosphines for ligand exchange reactions to induce chirality in the main chain of Pt-containing poly(aryleneethynylene)s (Fig. 16).[78] The chirality of BenzP* or QuinoxP* is transferred to the main chains of naphthalene- and carbazole-containing polymers after ligand exchange reactions, as confirmed by CD and UV–vis absorption spectroscopy. The chiral twist of the main chain is supported by the thermodynamic stability of the model compound for the monomer unit in the polymer, as well as the CD and UV–vis absorption spectra simulated by the DFT method. The QuinoxP*-based polymers emit photoluminescence, and the emission properties are reasonably explained by analyzing the MOs of singlet excited states of the model compound. Conformationally rigid Pt complexes feature CPL[79–86] and magnetic circularly polarized luminescence (MCPL).[87] Likewise, the Pt-containing polymers with BenzP* and QuinoxP* exhibit CPL and MCPL. Thus, the ligand exchange reaction is an efficient method to synthesize geometrically controlled Pt-functionalized optically active polymers from an optically inactive precursor polymer.

3. Development of functions

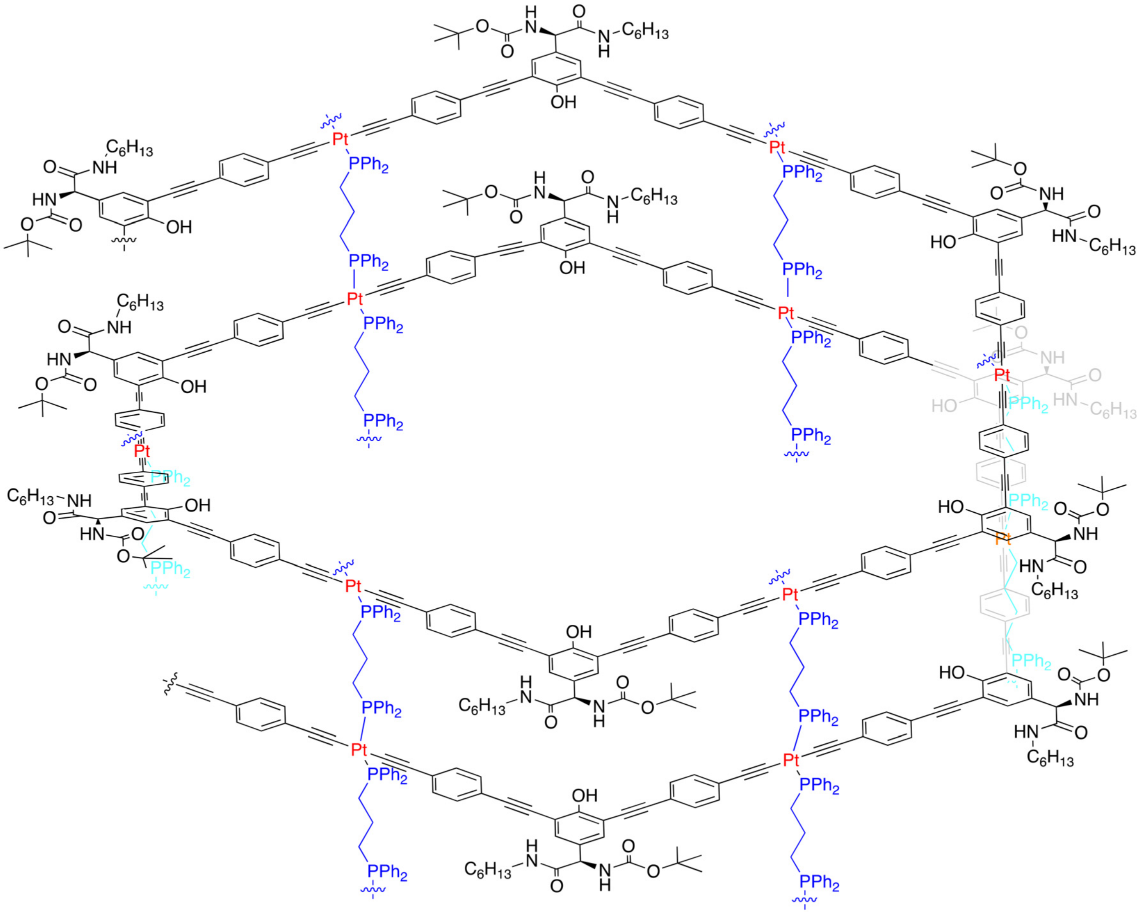
3.1 Catalysis

Hydrosilylation allows the addition of silicon hydrides to C=C, C=O and C≡C for the efficient synthesis of organosilicon compounds,[88] and is thus one of the most important reactions in organosilicon chemistry. It is widely used in industry for the production of silane coupling agents and silicone oils, rubbers and resins. Pt catalysts have been industrially used for hydrosilylation for over half a century because of their high stability against heat, oxygen and moisture, as well as their high catalytic activity and selectivity. The most important Pt catalyst in industry is Karstedt's catalyst, a Pt complex coordinated with 1,3-divinyltetramethyldisiloxane which was first investigated in the early 1970s.

Pt catalysis has reached a high level industrially. However, several drawbacks have been identified, including the formation of Pt black during hydrosilylation, leading to undesir-



Pt[$Ph_2P(CH_2)_2PPh_2$]-containing polymer



Pt[$Ph_2P(CH_2)_3PPh_2$]-containing polymer

Fig. 13 Possible structures of Pt[$Ph_2P(CH_2)_mPPh_2$]-containing polymers (m = 2, 3). Reprinted with permission from ref. 70. Copyright 2018 American Chemical Society.

able by-products and contamination of hydrosilylated products. Since it is commonly difficult to recover Pt catalysts from reaction mixtures and resins, the silicone industry consumes a large amount of this precious metal. Therefore, it is desirable to develop new Pt catalyst systems with recoverability as well as high efficiency and selectivity.

The development of polymer-supported metal catalysts has gathered attention from the viewpoint of recoverability and reuse.[89] Immobilization of transition metals on a polymer-support such as poly(styrene) has many advantages over the use of low-molecular-weight transition metal complexes. The supported metal complexes are ideally recovered from reaction mixtures by filtration without contaminating the products and can be reused. π-Conjugated polymers are also usable as supports for transition metal catalysts. Compared with poly(styrene)-supports, π-conjugated-polymer-supports possibly enhance the selectivity of products due to the conformational fixation of active sites based on rigid backbones.

Various attempts have been made to utilize poly(acetylene)s substituted with catalytic functional groups, including alkoxycarbene for phenylacetylene polymerization,[90] a Ru complex for asymmetric hydrogen transfer,[91] valine and *N*-methylvaline moieties for the reduction of aromatic ketimines,[92] and arylpyridyl-*N*-oxide for enantioselective allylation of benzaldehyde with allyltrichlorosilane.[93,94] Polyacetylenes with phosphine ligands in the side chains coordinate Pt to give crosslinked network polymers, which exhibit catalytic activity for hydrosilylation of 1-alkenes (Fig. 17, top).[95] Low-molecular-weight Pt catalysts favorably afford anti-Markovnikov adducts in hydrosilylation of 1-alkenes. On the other hand, the present Pt-containing polymers afford Markovnikov adducts at higher ratios, suggesting the possibility of control over selectivity of hydrosilylation by employing polymeric Pt catalysts. Polymers with Pt complex moieties in the main chain also exhibit catalytic ability in hydrosilylation.[96] Furthermore, Pt-graphene composite particles with diameters of 2–3 μm were prepared by sintering conjugated polymers containing Pt complexes, and their catalytic activities for alkene epoxidation (Fig. 17, bottom) and gas adsorption ability were examined.[97]

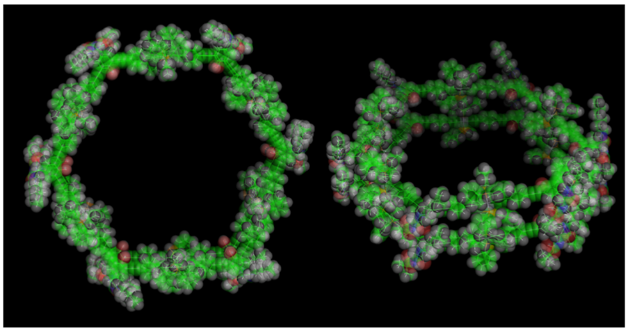


Fig. 14 Top and tilt views of a 12-mer model for a Pt[$Ph_2P(CH_2)_3PPh_2$]-containing polymer. Geometries were optimized by the DFT method [B3LYP/6-31G* (H, C, N, O, P)-LANL2DZ (Pt)]. Reprinted with permission from ref. 70. Copyright 2018 American Chemical Society.

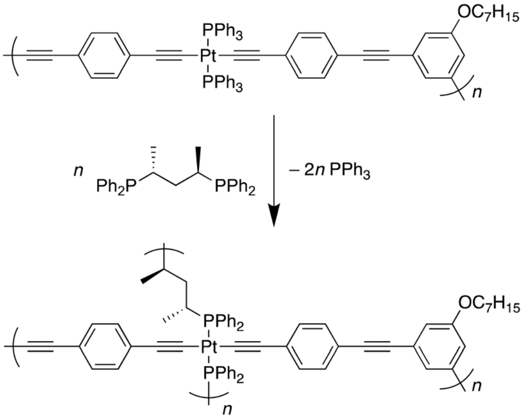


Fig. 15 Ligand exchange reaction of a $Pt(PPh_3)_2$-containing polymer with $Ph_2P–C^*H(CH_3)–CH_2–C^*H(CH_3)–PPh_2$ (*stereogenic center).

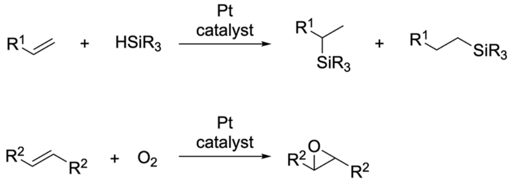


Fig. 17 Pt-catalyzed hydrosilylation (top) and epoxidation (bottom) of alkenes.

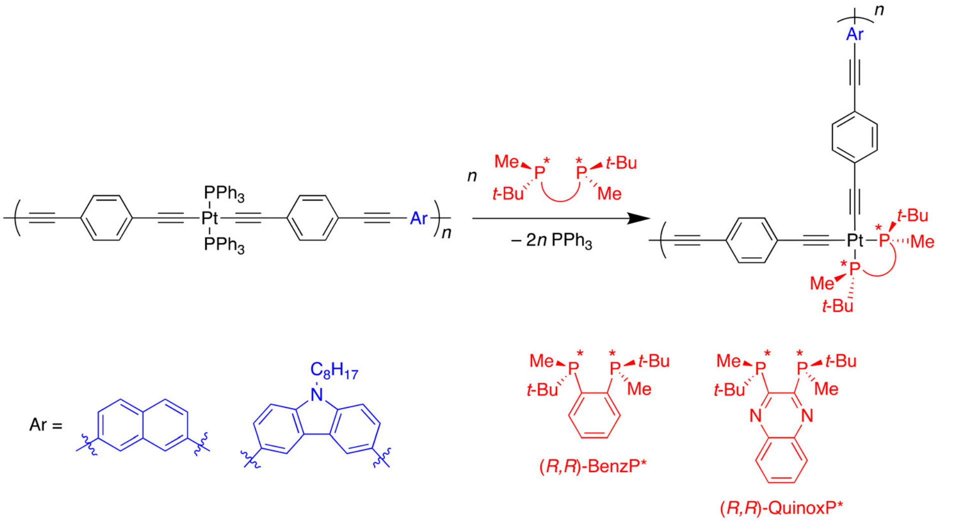


Fig. 16 Ligand exchange reaction of a $Pt(PPh_3)_2$-containing polymer with (*R*,*R*)-BenzP* and (*R*,*R*)-QuinoxP*.

3.2 Photon upconversion (UC)

Photon UC refers to the conversion of long-wavelength light into short-wavelength light, usually *via* sensitized triplet–triplet annihilation (TTA) using various combinations of chromophores ranging from the UV to near-infrared region.[98] TTA-UC is a practical way to convert low-energy photons into high-energy photons with sufficient energy for photovoltaic electron transfer. TTA-UC is mostly demonstrated in the solution state and in transparent polymer matrices like poly(methyl methacrylate), and in polymers that link sensitizing and emitter units covalently.[99] The Pt-acetylide complex is a promising TTA-UC sensitizer because it easily generates triplet excited states due to the heavy atom effect of Pt.

Ring-opening metathesis polymerization (ROMP) is a useful method for synthesizing polymers with precisely controlled molecular weight, dispersity and alignment of monomer units, allowing the introduction of various functional groups into polymers.[100,101] Some ROMP-based polymers are industrialized as transparent materials such as optical components for cameras. A series of amino-acid-functionalized poly(norbornene)s have been synthesized by ROMP,[102] some of which exhibit chirality recognition,[103] reverse micelle formation,[104,105] drug delivery capability,[106] and alternating sequence of carboxy- and amino-containing units.[107]

Poly(norbornene)s bearing Pt-acetylide complex moieties in the side chains have been synthesized *via* ROMP (Fig. 18, left),[108] while poly(norbornene)s bearing a Pt-acetylide complex moiety in the chain end were synthesized by ROMP of a norbornene monomer using the Grubbs 3rd generation catalyst. This was followed by a cross-metathesis reaction with a terminator[109] to obtain a polynorbornene bearing a Pt-acetylide complex moiety at the chain end (Fig. 18, right).[110] These polymers exhibited TTA-UC properties with excellent quantum yields (max 41%, with a theoretical upper limit of 50%), among the highest values of Pt compounds. Using acyclic diene metathesis (ADMET) polymerization, polymers containing Pt-acetylide complex moieties in the main chain have also been synthesized,[111] providing a new methodology for the molecular design of Pt-type polymeric sensitizers useful for photon TTA-UC.

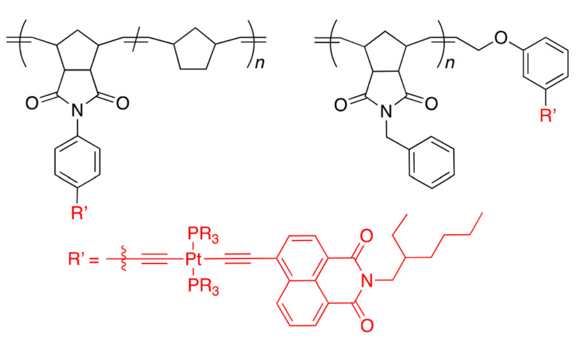


Fig. 18 Poly(norbornene)s bearing Pt-complex moieties in the side chains (left) and terminus (right).

3.3 CPL

In CPL, one circularly polarized beam is preferentially emitted. CPL materials have attracted attention due to their applicability in chirality recognition materials, light-emitting diodes, optical data storage, 3D displays, encryption and biological probes.[112] Among various organic and inorganic CPL molecules developed so far, organic lanthanoid complexes with bulky asymmetric ligands are promising because of the suppression of vibrational relaxation, prevention of nonradiative cross relaxation at diffusional collision, and asymmetric coordination geometry for enhancing electric dipole transitions.[113]

Chiral metal–organic frameworks (MOFs) are also expected to act as CPL materials.[114] The properties of MOFs are tunable by the metals and ligands. It is also possible to develop additional functions by utilizing the interaction between guest molecules and the host frameworks. MOFs are suitable for developing a wide variety of switching mechanisms and stimuli. The practical feasibility of MOFs as CPL materials will be increased by improving the stability over many switching cycles and switching speeds, and by increasing the sensitivity of their switching processes to chiroptical readout.

Nonpolymeric Pt complexes are also promising as CPL active materials,[115] including the *trans*-bis[(β-iminomethyl)naphthoxy]Pt complex (Fig. 19a)[85] and the axially chiral cyclometalated binuclear Pt complex (Fig. 19b).[116] Induction of helical π-conjugated structures (Fig. 19c) effectively enhances the CPL activity, resulting in a large luminescence dissymmetry factor (g_{lum}).[117] A Pt complex bearing tetraethylene glycol (Fig. 19d) exhibits a significantly larger g_{lum} in the liquid state than that in the solution state, and is expected to be a solvent-free CPL material.[118] Solvent-free CPL systems can also be achieved by embedding Pt complexes in transparent plastic films like PMMA. Some CPL-active polymers containing metal complex moieties have been reported, including helical poly(acetylene)s substituted with fluorescent dansyl groups and amino groups that coordinate metal ions,[119] poly(ethylene glycol)-*block*-poly(L-glutamic sodium) with a cationic gold(I) complex in the side chains,[120] and supramolecular polymers formed by the assembly of bis(phenylisoxazolyl)benzenes connected with Pt complexes.[121] There is a need for further development of polymeric materials containing metal complexes that are fabricated in films, especially from the viewpoint of formability and processability for practical usage. Achiral late transition metal complexes exhibit CPL by the application of magnetic fields, which remarkably widen the possibility for CPL materials.[115]

3.4 Mechanochromism

Mechanochromic polymers show color changes in response to external mechanical stimuli.[122–124] The most prominent examples include materials that display visual warning signs upon strain as indicators of mechanical failure, and stress-sensitive sensors that indicate deformation or failure. Visualizing the mechanical stress on polymeric materials is useful for

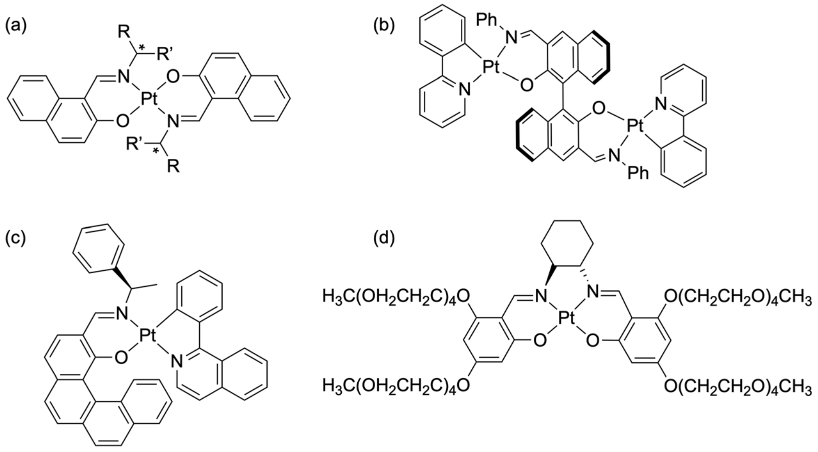


Fig. 19 CPL active Pt complexes (a)–(d).

understanding the fundamental processes of stress transfer and mechanical failure in polymeric materials.

Various fluorescent and phosphorescent mechanisms have been utilized to achieve efficient mechanochromism. Planar Pt complexes, such as Pt complexes with phenylpyridine, bipyridine and phenanthroline ligands, are promising as mechanochromophores because they stack, especially in the solid state, mainly due to Pt⋯Pt interaction. The degree of stacking is tunable by mechanical stimuli, leading to changes in metal–ligand charge-transfer (MLCT), metal-to-metal charge-transfer (MMCT), metal–metal-to-ligand charge-transfer (MMLCT) and ligand-to-ligand charge-transfer (LLCT) resulting in visible changes in the absorption and/or emission spectra. Pt complexes containing aza-crown dithiocarbamate moieties (Fig. 20a) exhibit mechanochromic luminescence upon grinding, and mechanochromic reversibility toward various solvents.[125] Polynuclear –(Pt–Tl)$_n$– complexes (Fig. 20b),[126] bis(phenylpyridine) Pt complexes (Fig. 20c),[127] (bis((alkyloxy) phenyl-pyridinyl)pyrazolate) Pt complexes (Fig. 20d)[128,129] and bis(*N*-methylbenzimidazolyl)pyridine Pt complexes (Fig. 20e)[130] exhibit aggregation-induced emission in PMMA films that exhibit mechanochromism.

Mechanochromic polyurethane elastomers are expected to be next-generation rubber elastic materials that exhibit excellent mechanical strength, abrasion resistance, and flexural resistance, as well as easy detection of defects.[131–134] Bipyridine-Pt-acetylide-containing polyurethanes exhibit a fluorescent color change upon abrasion (Fig. 21).[135] Furthermore, segmented polyurethanes have been synthesized using the Pt-containing diol monomer. The polyurethanes exhibit mechanical properties comparable to those of common polyurethane elastomers, as well as reversible orange and yellow luminescent color changes upon tensile stress and relaxation. The mechanochromic polyurethanes are expected to be applied to textile

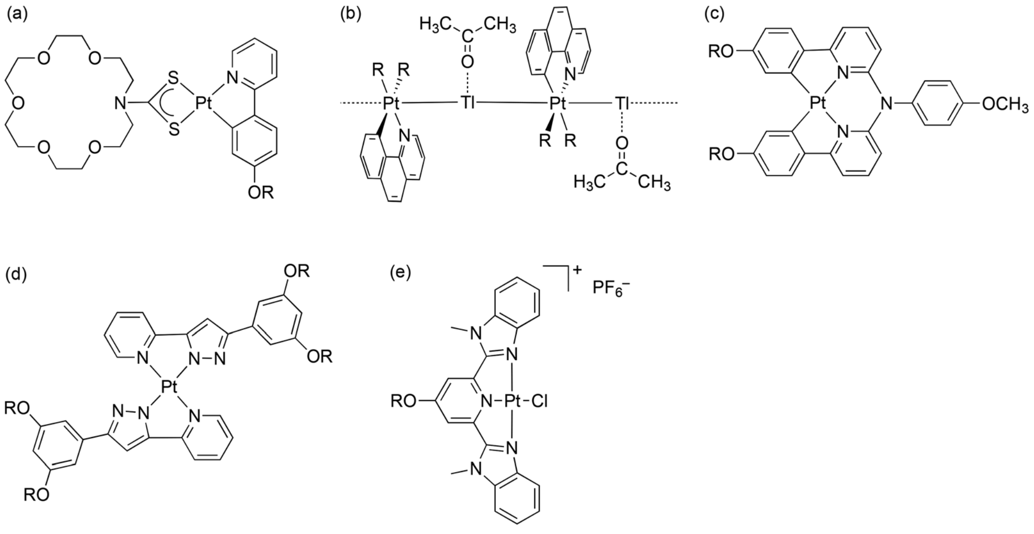


Fig. 20 Pt complexes (a)–(e) exhibiting mechanochromism.

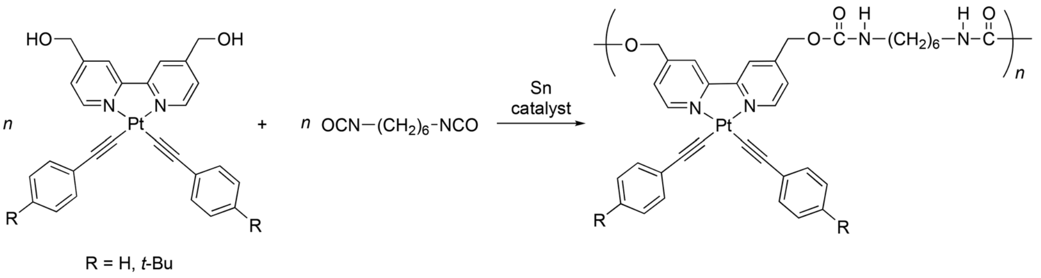


Fig. 21 Synthesis of mechanochromic polyurethanes bearing Pt complex moieties.

fabrics such as polyesters, in which a fluorescent color change enables easy detection of defect areas.

3.5 Chiral recognition

Molecular recognition is essential for living systems because it allows biomolecules to interact with each other and with other compounds and is involved in many biological functions, including gene transfer and reproduction, tissue and organ formation, and immune response. Chiral recognition, which identifies molecular asymmetry, provides the basis for organic synthetic chemistry such as catalytic asymmetric synthesis. Chiral recognition is also important in materials science as well as in biochemistry. Polymers recognizing chirality are promising materials that are applicable in separation technologies as constituents of chiral columns.[136,137] Optically active π-conjugated polymers, such as chirally substituted poly(acetylene)s, poly(thiophene)s and poly(aryleneethynylene)s, are actively investigated for chiral recognition because the chiroptical properties vividly respond to the interaction with chiral molecules.[138] Due to its high sensitivity, CD spectroscopy analysis is commonly employed to examine the chiral recognition ability of π-conjugated polymers.

2,2′-Bipyridine is widely used as a bidentate ligand to form stable planar transition metal complexes. Amino-acid-derived optically active poly(phenyleneethynylene)s containing bipyridine-Pt complexes (Fig. 22) form chirally ordered aggregates, which exhibit intense circular dichroism (CD).[139] Pt–Pt, Pt–π, hydrogen bonding, and van der Waals interactions synergistically drive aggregation.[77,140,141] Optically active bipyridine-containing poly(phenylene ethynylene)s using an amino alcohol as a chiral source form a folded structure as single molecules. They also form aggregates,[142] as shown by CD and UV–vis absorption spectroscopy, dynamic light scattering, quantum chemical calculations, and molecular dynamics simulations. Films of these polymers exhibit differences in contact angles of 10–20° with aqueous solutions of (*R*)- and (*S*)-alcohols. The trend of these differences is comparable to the differences in the calculations of solvation free energies. When various metal chlorides or metal perchlorates were added to polymer solutions, quenching and changes in luminescence color were observed, depending on the identity of the metal. It is assumed that metals coordinate to the bipyridine moieties to change the configurations and conjugation length. The polymers are expected to be applied in metal sensing materials.

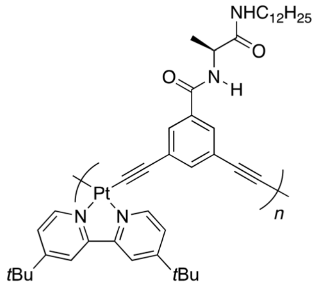


Fig. 22 Optically active poly(phenyleneethynylene) bearing bipyridine-Pt-complex and amino-acid moieties.

4. Conclusions

This article provides an overview of the synthesis and structural control of coordination polymers containing conjugated transition metal complex moieties, primarily Pt complexes, and their applications. Those polymers adopt predominantly one-handed helical conformations, and chirally they become aggregated by the incorporation of functional groups causing intra- and intermolecular π-stacking, hydrogen bonding and van der Waals interactions. A wide variety of polymers containing Pt-acetylide complex moieties in the main chain have been synthesized by dehydrochlorination coupling polymerization of PtL_2Cl_2 with bisethynyl compounds and by chain polymerization of monomers bearing a Pt-acetylide complex moiety. A series of polymers including poly(phenyleneethynylene)s, poly(norbornene)s and poly(acetylene)s with conjugated transition metal complex moieties have been synthesized to clarify the effect of ligands on main chain conjugation and the methodology for controlling higher-order structures by utilizing ligand interactions. Chiral higher-order structures are induced based on the control of geometric structures at the Pt center and intramolecular bridging reactions by exchanging phosphine ligands. The metal-containing polymers exhibit useful functions including catalysis, photon upconversion, asymmetric recognition, metal sensing, and mechanochromism.

Thus, metal-containing polymers have a wide range of applications in fields such as electronics, catalysis, and biomedicine due to their electronic, magnetic, and optical properties. However, there are some issues that should be considered in metal-containing polymers. First, it is difficult to control the structure precisely. Metal-containing polymers are composed of metal complexes that consist of metals and organic ligands, making it difficult to control their uniform structure. This results in issues with reproducibility of the physical properties. Second, some metal-containing polymers are unstable to oxidation, moisture and light, making them difficult to be used or stored over long periods of time. Third, delicate processing technologies are necessary for practical applications, such as molding and film formation. Fourth is environmental and cost issues. When noble metals are contained, costs may be high, and environmental impact may be a concern.

Future development of metal-containing polymers largely depends on the advancement of molecular design. Advances in computer simulation and molecular design technologies are expected to lead to the development of novel metal-containing polymers with optimized properties. Applications as multifunctional materials with specific functions, such as electronic devices, energy storage materials, and biosensors, are expected to progress. The use of environmentally friendly metal elements and recyclable material design will become important themes. Combining control technology for nanostructures is also expected to lead to the realization of novel properties, which may be difficult with conventional materials. Thus, metal-containing polymers are expected to play an increasingly diverse role in various fields based on the progress both of basic and applied research.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

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