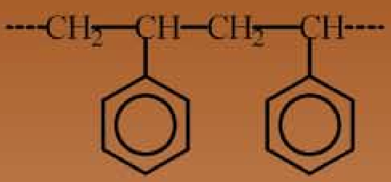
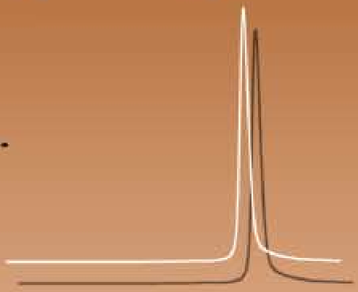


Hermann Staudinger

$$\text{----}CH_2-CH_2-\overset{\displaystyle CH_3}{C}=CH-CH_2-CH_2-\overset{\displaystyle CH_3}{C}=CH\text{----}$$



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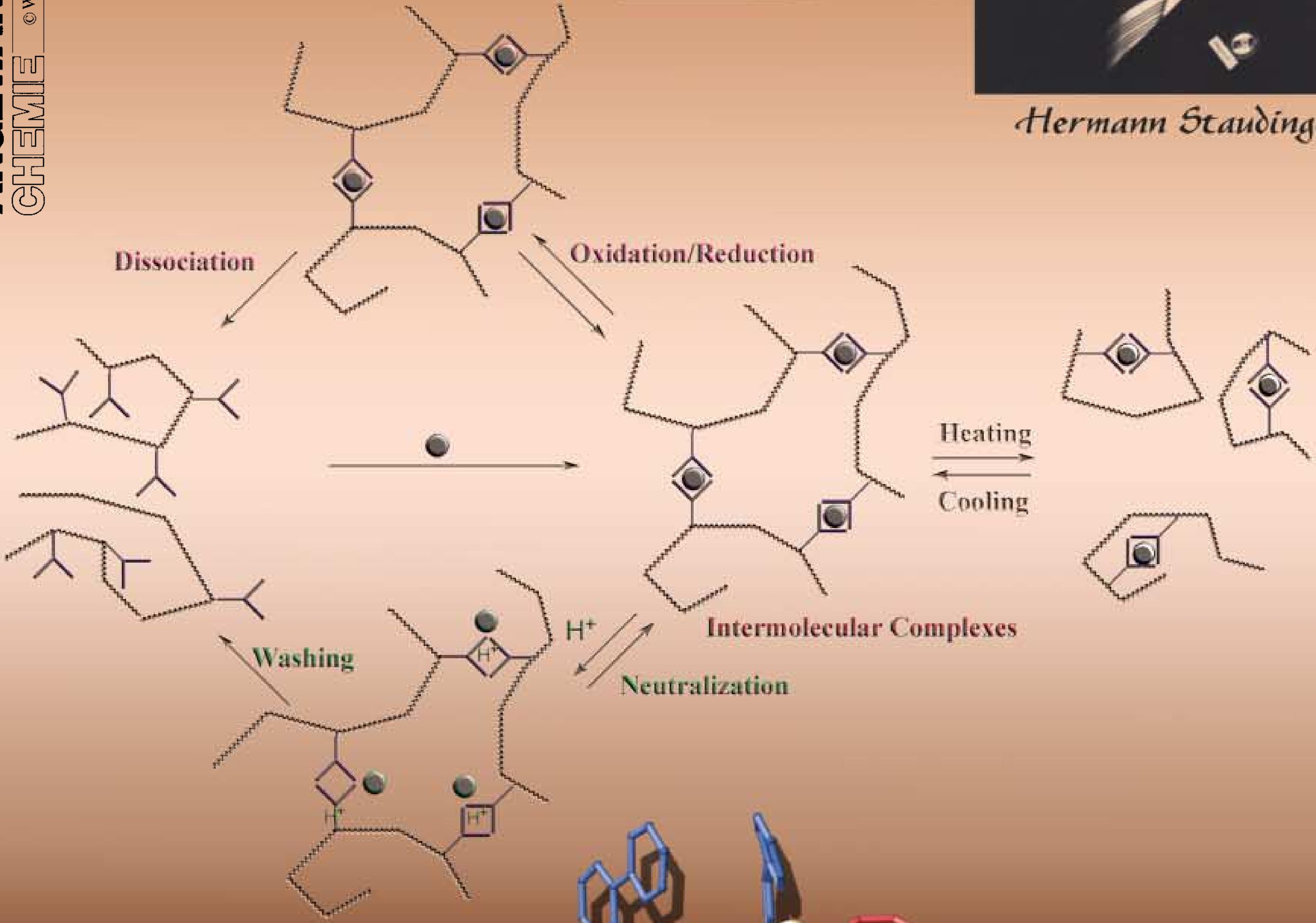

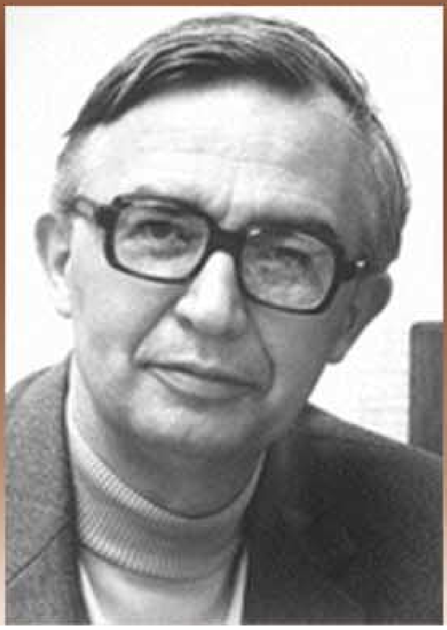

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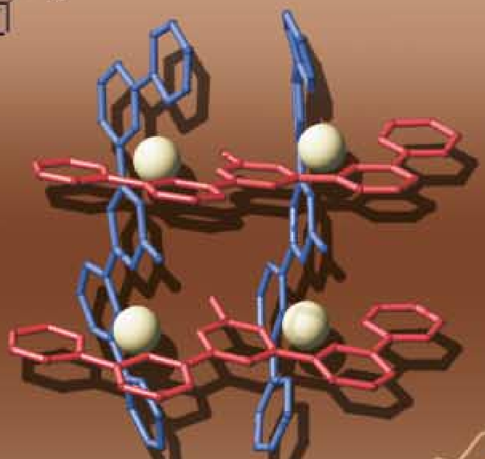

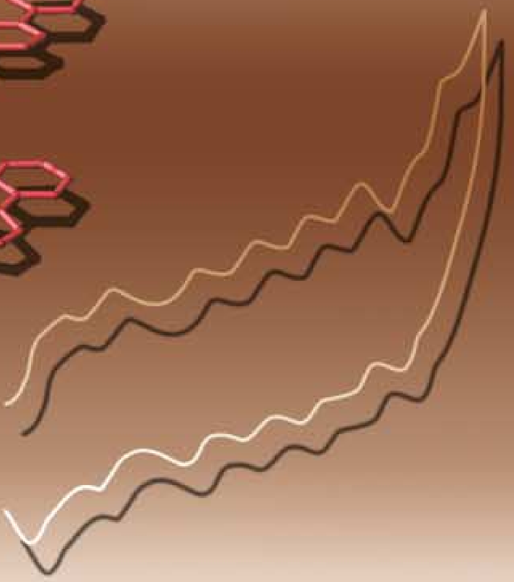

Macromolecules Containing Bipyridine and Terpyridine Metal Complexes: Towards Metallosupramolecular Polymers

Ulrich S. Schubert* and Christian Eschbaumer

Dedicated to Professor Dr. Claus D. Eisenbach

The ability of a broad range of N-heterocycles to act as very effective and stable complexation agents for several transition metal ions, such as cobalt(II), copper(II), nickel(II), and ruthenium(II), has long been known in analytical chemistry. This behavior was later utilized in supramolecular chemistry for the construction of highly sophisticated architectures, such as helicates, racks, and grids. The discovery of macromolecules by Staudinger in 1922 opened up avenues towards sophisticated materials with properties hitherto completely unknown. In the last few decades, the combination of macromolecular and supramolecular chemistry has been attempted by developing metal-complexing and metal-containing polymers for a wide variety of applications that range from filtration to catalysis. The stability of the polymer–metal complex is a fundamental requirement for such applications. In this respect, the use of bi- and terpyridines as chelating ligands is highly promising, since these molecules are known to form highly stable complexes with interesting physical properties with transition-metal ions. A large number of different structures have been designed for many different applications, but polymers based on the application of coordinative forces have been prepared in a few cases only. Furthermore, the synthetic procedures applied frequently resulted in low yields. During the last few years, strong efforts have been made in the direction of self-assembling and supramolecular polymers as novel materials with "intelligent" and tunable properties. In this review, an overview of this active area at the interface of supramolecular and macromolecular chemistry is given.

Keywords: bipyridine ligands · coordination chemistry · polymers · supramolecular chemistry · terpyridine ligands

1. Introduction

Since 1987, when Lehn, Pedersen, and Cram received the Nobel prize for their studies in selective host–guest chemistry,[1–3] supramolecular chemistry has become a well-known concept and a major field of today's chemical research. Starting with the development and design of crown ethers, spherands, and cryptands, modern supramolecular chemistry concerns the self-assembly[4] of well-defined structures, similar to those in natural systems.[5] In the same time frame, there was a blending of supramolecular systems with tailor-made macromolecules and traditional polymer chemistry. By making a supramolecular entity with a relatively large polymer ratio, it is possible to produce on a large scale materials combining the new and interesting features and structures of supramolecular species with well-known polymeric properties. As a consequence of their polymeric nature, these materials can be, for example, spin-coated into thin films or used in bulk systems, thus reducing technical processing to common techniques used in polymer engineering. By altering the polymer part, the macroscopic properties of the material can be changed dramatically, for example, from rigid to elastic, from hydrophobic to hydrophilic, or from liquid to solid. A prominent example of the combination of hydrogen bonding and polymer chemistry is represented by the work of Meijer's research group:[6] the creation of stable polymers built up from low-molecular-weight poly(ethylene/butylene) with telechelic 2-ureido-4[1*H*]-pyrimidinone end groups. The end groups bind each other by quadruple hydrogen bonds which results in supramolecular high-molecular-weight polymers. Since the polymerization is reversible, a strong temperature dependence of the melt viscosity was detected because of depolymerization. The current research results in this area have been summarized in a recent review.[7]

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[*] Prof. Dr. Ulrich S. Schubert, Dr. C. Eschbaumer
Laboratory of Macromolecular and Organic Chemistry
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven (The Netherlands)
Fax: (+31) 40-247-4186
E-mail: u.s.schubert@tue.nl

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In this review we consider the results of a different combination story: that of metal complexes (metallosupramolecular assemblies) with polymer chemistry and materials.[8] In view of the outstanding importance of 2,2′-bipyridine and 2,2′:6′,2″-terpyridine ligands (Figure 1) and metal complexes, we have limited this review to macromolecules and polymers containing these types of ligands or their metal complexes. Polymers containing the bipyridine analogue phenanthroline will not be considered here (for an overview see ref. [9]). For other general overviews concerning metal-containing polymers see, for example, refs. [9–12].

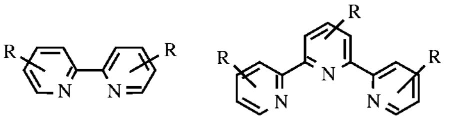


Figure 1. 2,2′-Bipyridine and 2,2′:6′,2″-terpyridine.

Since 2,2′-bipyridines are considered only in this review we will call them simply bipyridines and adopt the abbreviation bpy for these ligands. Bipyridines have been known since 1888 when F. Blau synthesized the first bipyridineiron complex.[13] One year later, Blau synthesized and analyzed bipyridine by dry distillation of copper picolinate.[14] Since the molecule consists of two identical parts, no directed coupling procedure is required for its synthesis. Therefore, unsubstituted and symmetrically substituted (in particular, 4,4′-functionalized) bipyridines are accessible in good yields. Apart from this, bipyridine–metal complexes (in particular ruthenium complexes) have very interesting photochemical and other properties which, for example, makes them suitable for applications in solar energy conversion.[15] For these reasons, scientists started in the early 1970s to insert bipyridine units into polymers, thin films, and membranes. A large part of the review is therefore devoted to this theme.

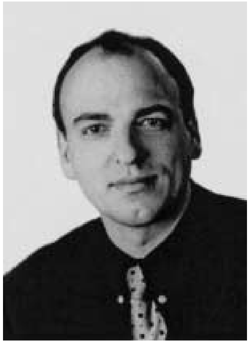
The chemistry of 2,2′:6′,2″-terpyridines (here simplified to terpyridine and abbreviated as tpy) is much younger than that of bipyridines. Terpyridine (Figure 1) was isolated for the first time by Morgan and Burstall in the 1930s.[16, 17] The molecule contains three nitrogen atoms and can therefore act as a tridentate ligand and form stable complexes by chelating a broad variety of transition metal ions.[18, 19] This property has been widely used in analytical chemistry.[18] Nevertheless, it took almost 30 years longer than a bipyridine-containing polymer for the first example of a terpyridine-containing polymer to be published. This time difference can be attributed to the difficulty in preparing terpyridines, particularly substituted terpyridines. Overviews of metallodendrimers with complex building units other than bi- and terpyridines can be found in refs. [20, 21].

2. Macromolecules Bearing Bipyridine Units

2.1. Dendrimers and Starlike Macromolecules

In 1999, Newkome et al. published a very detailed review on metallodendrimers and metal-containing starlike marcomolecules.[20] There have been many publications on macro-

Ulrich S. Schubert was born in Tübingen (Germany) in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth and the Virginia Commonwealth University, Richmond (USA). His Ph.D. work was performed under the supervision of Professor C. D. Eisenbach (Bayreuth, Germany) and Professor G. R. Newkome (Florida, USA). In 1995 he obtained his doctorate with Prof. Eisenbach. After a postdoctoral training with Professor Lehn at the Université Strasbourg (France) he moved to the Technische Universität München (Germany) where he obtained his habilitation in 1999 (with Professor O. Nuyken). From 1999 to spring 2000 he held a temporary position as a professor at the Center for NanoScience at the Universität München (Germany). Since summer 2000 he has been a Full-Professor at the Eindhoven University of Technology. His awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Makromolekulare Chemie), the Heisenberg Stipendium of the DFG and the Dozenten Stipendium of the Fonds der Chemischen Industrie. The major focus of his research interests relates to organic heterocyclic chemistry, supramolecular materials, nanoscience, combinatorial material research, and tailor-made macromolecules.



U. S. Schubert

C. Eschbaumer

Christian Eschbaumer was born in 1970 at Erding (Germany). He started studying chemistry at the Technische Universität München in 1991. His diploma thesis dealt with the synthesis of functionalized terpyridines as building blocks for heavy-metal-complexing polymers. In 1998 he started working on his Ph.D. thesis at the Technische Universität München in the group of Prof. U. S. Schubert with a project entitled "Metallo-Supramolecular Polymers—On the Way to New Materials". From July 2000 he continued his work at the Technische Universiteit Eindhoven, where he defended his thesis in March 2001. In October 2000 he joined the Memory Products Division of Infineon Technologies (Erlangen/Germany).

molecules with bipyridines attached only to the outermost sphere of the molecule to saturate the free coordination sites of a metal complex (for example, in ref. [20, 21]). In this review, only selected dendrimers and some starlike molecules are discussed. We will divide this part into two sections. Dendrimers with bipyridine–metal complexes within its core are discussed followed by starlike molecules containing either complexed or free bipyridine ligands at the surface.

The work of Newkome et al. fits just in between these two sections.[22] They incorporated a 5,5″-diamino-functionalized bipyridine through ester binding onto the backbone of two molecules (Figure 2). The addition of a bis(bipyridine)ruthenium(II) complex resulted in systems in which tris(bipyridine)ruthenium(II) complexes are bound within the inner sphere of the dendrimer, but do not act as branching units. These systems consist of the same core, but their surfaces differ.

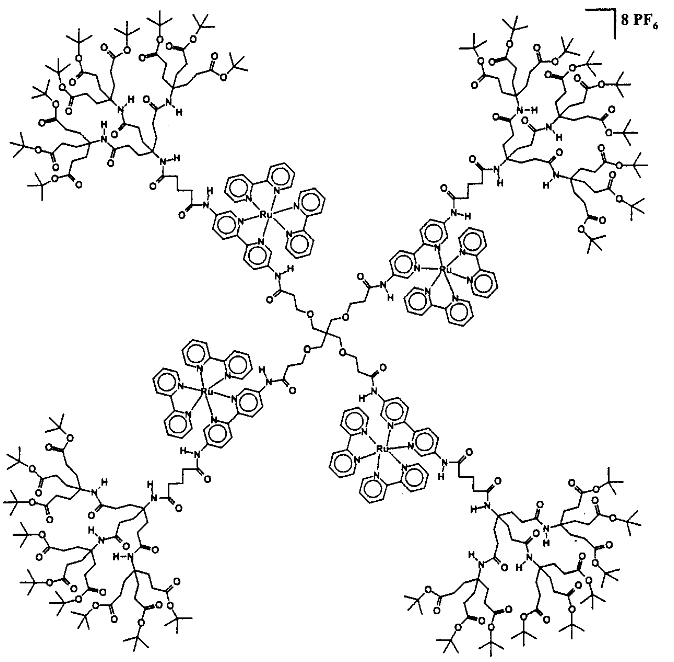


Figure 2. The dendrimer synthesized by Newkome et al. contains metal complexes within the inner sphere of the molecule.[22]

Dendrimers containing a bipyridine–metal core are rare. In 1991, Beer et al. reported a starlike system with a tris(bipyridine)ruthenium(II) core and six benzo- or azacrown ether units on the surface (Figure 3).[23] The alkynyl- or vinyl-linked systems are electropolymerizable and produce films capable of recognizing alkali and alkaline-earth metal cations (as shown by spectroscopic methods). The ligand-centered absorption band and the metal→ligand charge-transfer (MLCT) emission maximum of both the monomer and polymer films were shifted to lower wavelengths in the presence of these ions. A typical value for the shift in the spectrum of a monomeric complex is 16 nm (from 686 to 670 nm).

Vögtle, De Cola, and Balzani et al. also used a convergent strategy to assemble five different types of dendrimers up to the third generation with bipyridineruthenium complexes forming the core.[24–26] The aim of this work was the design of photoactive and redox-active dendrimers by the incorporation of bipyridine complexes. The large dendritic complexes exhibited more-intense emission and a longer excited state lifetime than common [Ru(bpy)$_3$] complexes. For example, the excited-state lifetime of the dendrimer with 54 peripheral methyl ester units in aerated acetonitrile solution is longer than 1 μs. The structures of the dendritic ruthenium complexes have been deduced by using NMR spectroscopy and MALDI-TOF mass spectrometry. Another example of a dendrimer with a tris(bipyridine)ruthenium(II) core was reported by Constable et al.[27, 28]

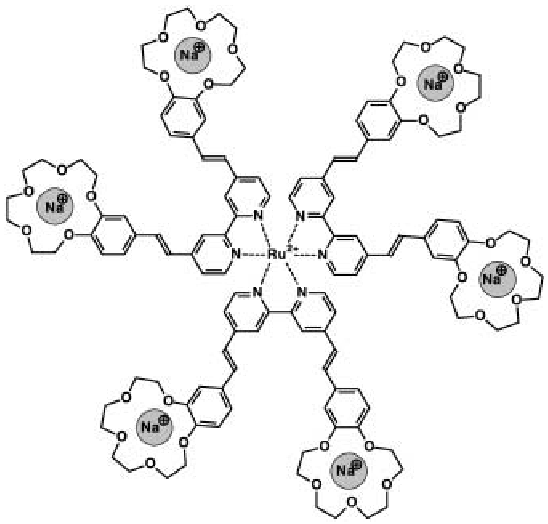


Figure 3. Alkali and alkaline-earth metals can be recognized by the benzocrown ether with a [Ru(bpy)$_3$] core synthesized by Beer et al.[23]

In 1997, Marvaud and Astruc presented starlike macromolecules containing either benzene or [(η^5-C$_5$H$_5$)Fe^{II}-(η^6-C$_6$R$_6$)] (R = CH$_3$) as the core and pyridine, bipyridine, terpyridine, or the corresponding ruthenium complexes at the surface.[21] A divergent approach (Figure 4) was used for constructing the molecules. The characterization of molecules with up to 12 positive charges was performed by NMR spectroscopy and also by MALDI-TOF and electrospray mass spectrometry. Further evidence for the presence of terminal Ru complexes was obtained by electrochemical measurements, where the Ru^{II}/Ru^{III} redox systems gives a single and reversible anodic wave at +0.82 and +0.79 V (versus the ferrocene/ferrocenium couple (Fc/Fc$^+$)).

Some innovative work in this direction has been reported by Abruña's research group with their poly(amidoamine)-based dendrimers containing pendant bipyridine- or terpyridineruthenium complexes (see Section 3.1).[29–31] The research groups of Puddephatt, Achar, and Catalano chose a divergent route to synthesize organoplatinum or mixed organoplatinum/palladium dendrimers.[32–36] The dendrimers were built up converting a four-coordinate, square-planar platinum(II) center into a six-coordinate, octahedral platinum(IV) center by oxidative addition of an aryl bromide to the repeat unit. Figure 5 shows an organoplatinum dendrimer with four arms in which transition metal ions are present in every layer of the dendrimer except in the core. Up to 12 ferrocene units have been incorporated in one macromolecule.[36]

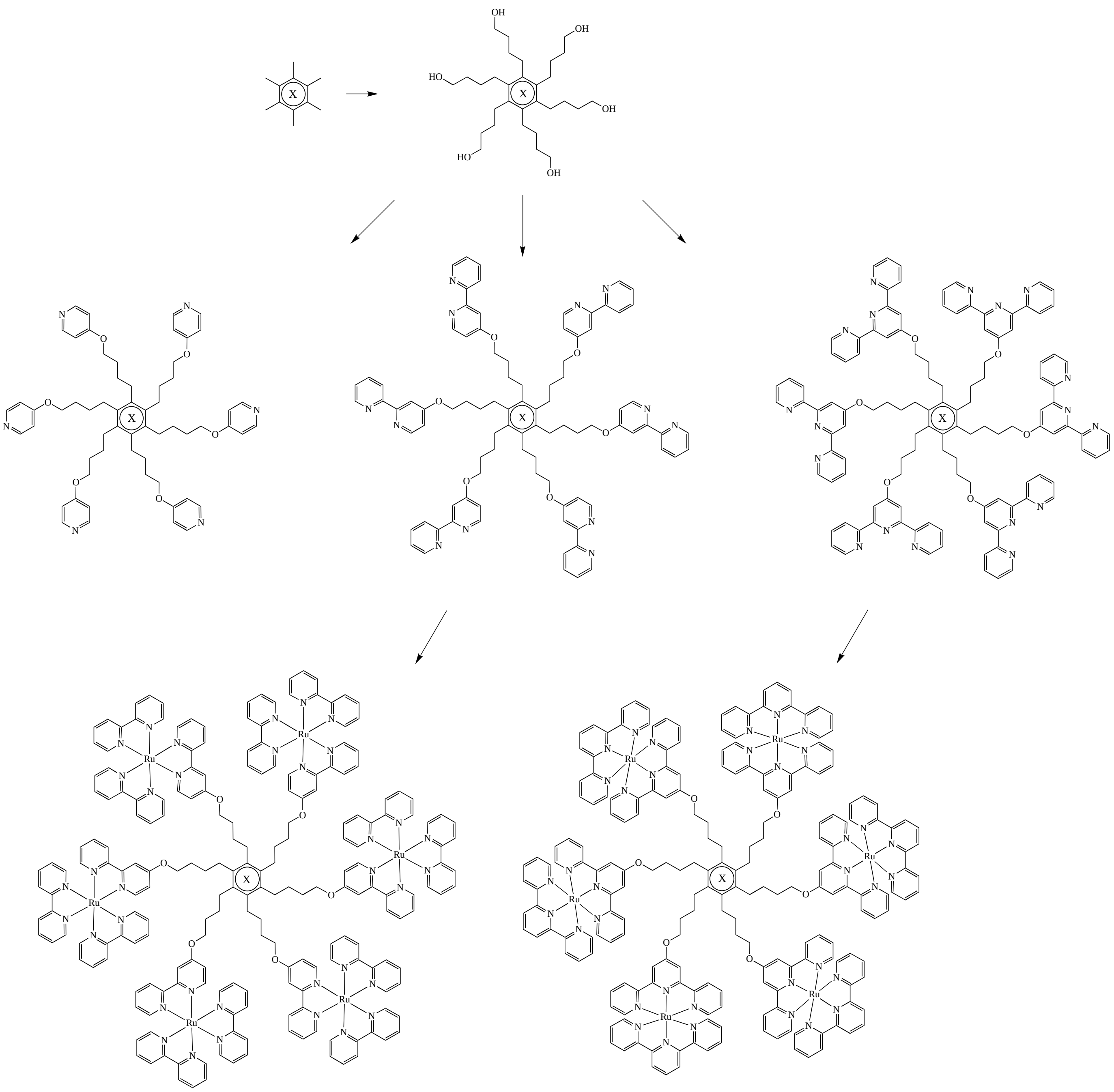


Figure 4. Synthesis of $[Ru(bpy)_3]$-terminated macromolecules with a metallocene core ($X = Fe(\eta\text{-}C_5H_5)^+$) by Marvaud and Astruc.

2.2. Polymers with Bipyridine Units in the Side Chain

Kaneko et al. presented their first studies on polymers with covalently bound bipyridines in 1980.[37, 38] They targeted the preparation of a heterogeneous photocatalyst for the decomposition of water by solar irradiation. The polystyrene backbone was radically polymerized, then brominated, lithiated, and finally treated with bipyridine in different molar ratios (Figure 6). The resulting modified polymers were characterized by IR and UV/Vis spectroscopy. The photochemical reduction of methyl viologen revealed the existence of three components in the polymer with lifetimes τ of the excited state $[Ru(bpy_3)]^{2+*}$, ranging from 7 to 474 ns.[39] The rate constant k_1 for the transition from the excited state complex to methyl viologen MV^{2+} was determined to be around $10^8\,L\,mol^{-1}s^{-1}$, as in monomeric complexes.

As a next step, Kaneko et al. prepared *p*-aminostyrene-*N*-vinylpyrrolidone copolymers with pendant tris(bipyridine)-ruthenium(II) complexes (Figure 7).[40] Again, the polymer backbone was synthesized first. Afterwards it was treated with 2,2′-bipyridine-4,4′-dicarboxylic acid to form the corresponding amides. Ruthenium complexes were obtained by subsequent reaction of the polymer with $[Ru(bpy)_2CO_3]$. In 1982, Kaneko et al. also investigated the copolymerization of 4-methyl-4′-vinylbipyridine with styrene,[41] followed by analogous work with a variety of other co-monomers such as

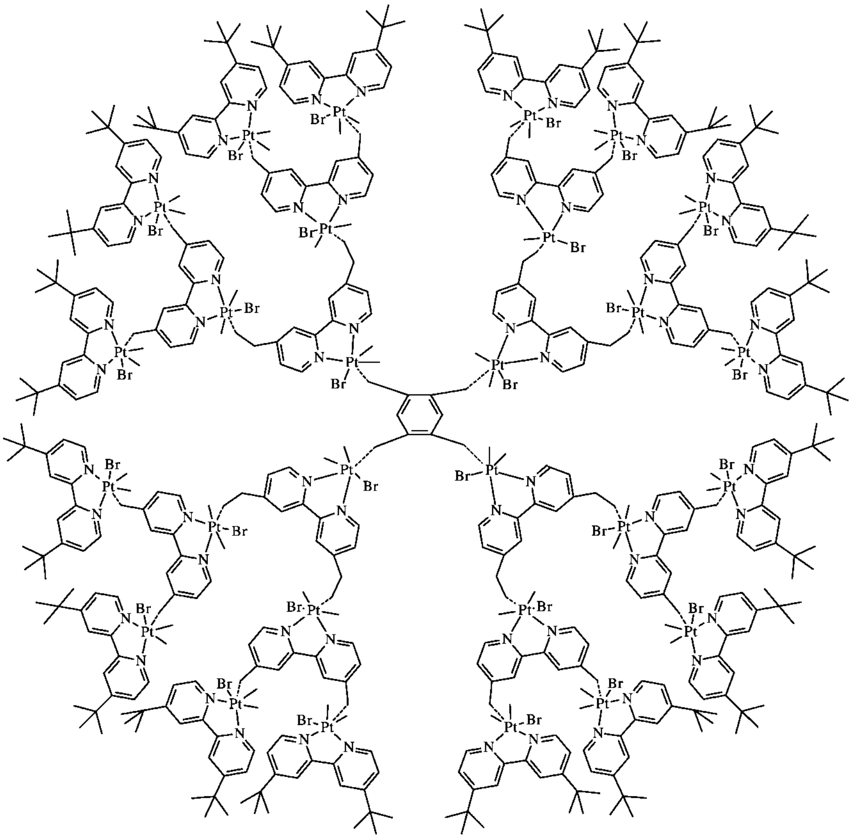


Figure 5. Organoplatinum dendrimer with four dendrons.[33, 34]

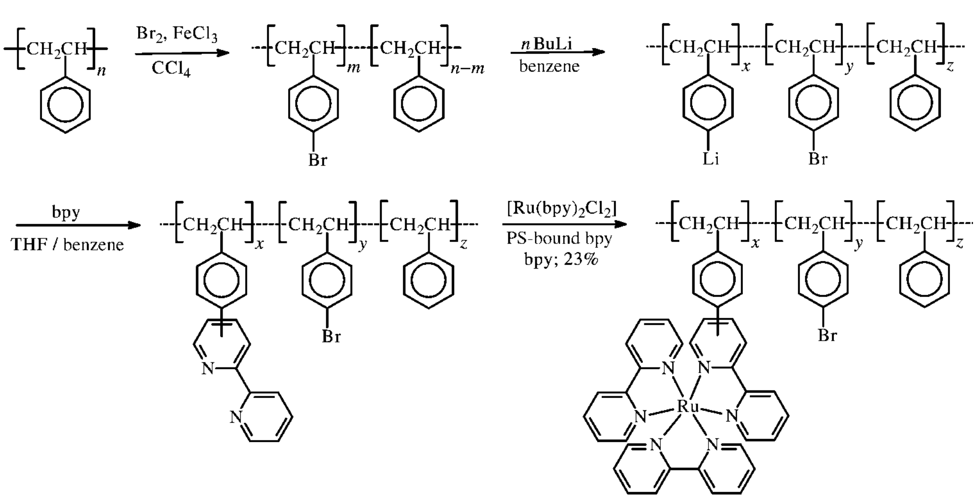


Figure 6. Synthesis of the first polymers with pendant [Ru(bpy)3] complexes.[37, 38]

acrylic acid, methyl methacrylate, and *N*-vinylpyrrolidone.[42–46] A lifetime τ of 430 ns and a rate constant k_1 of $10^8\,\mathrm{L\,mol^{-1}s^{-1}}$ were determined for the excited states of the complexes. The influence of the anionic and cationic pendant groups on the quenching of the photoexcited state were later studied.[42–45]

Another contribution aimed at the photochemical conversion of solar energy was made by Sumi et al.[47] They synthesized 6-vinylbipyridine and 4-methyl-4′-vinylbipyridine (Figure 8a, b), and used free-radical polymerization to prepare the corresponding homopolymers. While poly(4-methyl-4′-vinylbipyridine) was insoluble because of cross-linking, poly(6-vinylpyridine) was soluble in common organic solvents. After complexation with different transition metal chlorides, poly(6-vinylbipyridine) became soluble in water and insoluble in THF, while the cross-linked poly(4-methyl-4′-vinylbipyridine) swelled to a voluminous gel. In an alternative monomer synthesis, Pd-catalyzed coupling of pyridine-*N*-oxide was used instead of copper catalysis to prepare 4-methyl-4″-vinylbipyridine (Figure 8c).[48] The poly(4-methyl-4′-vinylbipyridine) produced from this monomer was found to be soluble in common organic solvents.

First investigations on the use of bipyridine–metal complexes as templates for polymeric matrices were carried out by Gupta and Neckers in 1982.[49] The idea was to copolymerize divinylbenzene and metal complexes of 4′-methyl-4-vinylbipyridine in variable quan-

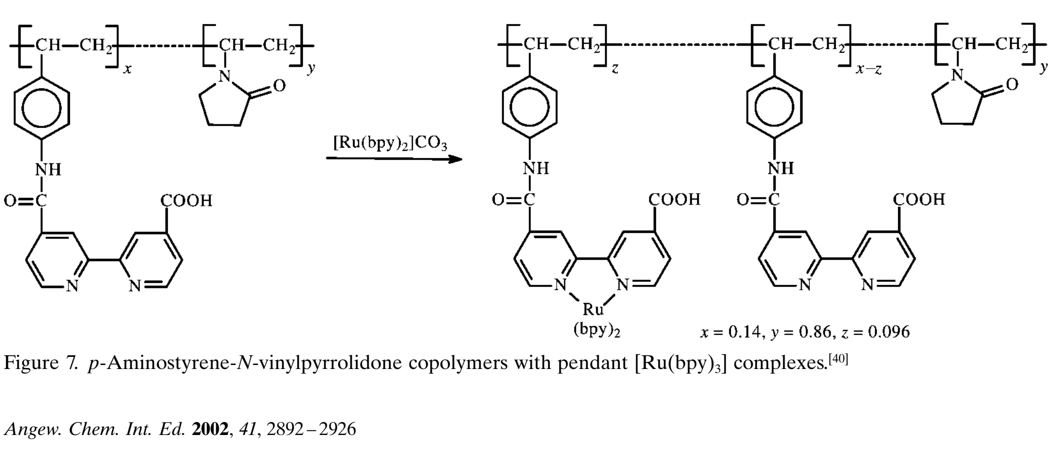


Figure 7. *p*-Aminostyrene-*N*-vinylpyrrolidone copolymers with pendant [Ru(bpy)3] complexes.[40]

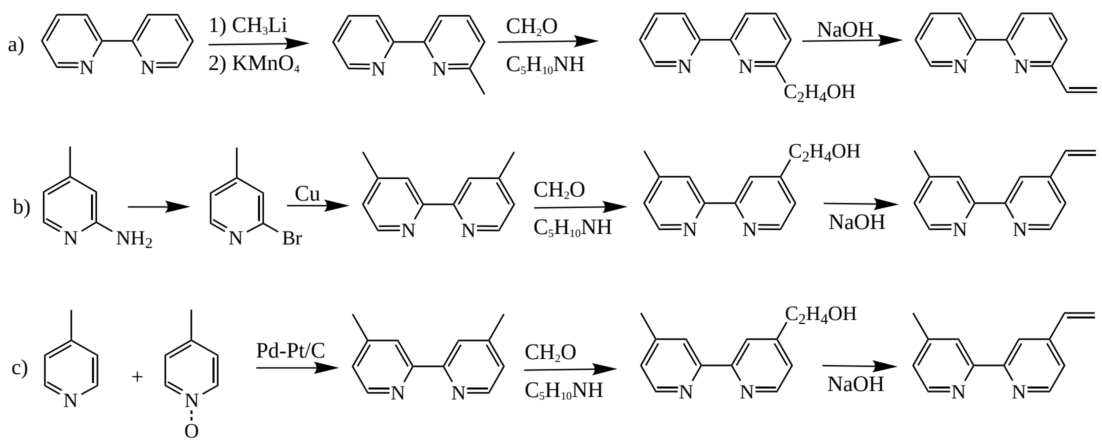


Figure 8. Vinyl-substituted bipyridines as monomers for radical polymerization.[47, 48]

tities, to remove the metal ion, and then to measure the selectivity of the polymer for the metal ion (Figure 9). This system demonstrated some template effect but on a too small a scale to be of relevance for practical applications.

In 1982, Kelly and Tinnemans et al. reported on the photo- and electrochemical properties of polymer-bound bipyridineruthenium and bipyridinetungsten complexes. The copolymers were prepared from 6-styrenebipyridine and styrene, methyl methacrylate, or maleic anhydride and treated with ruthenium or tungsten ions.[50] In contrast to the results from the studies of Kaneko et al., the authors detected that the rate of production of methyl viologen MV^+ was only slightly greater in the presence of the Ru^{II} complexes than in their absence, which suggests that the different sites of attachment might be responsible for the results. In 1984, Fischer investigated the preparation of bipyridines with long-chain substituents by deprotonation of 4,4′-dimethylbipyridine with lithium diisopropylamide (LDA), and then addition of bromododecane or poly(vinylbenzyl chloride).[51]

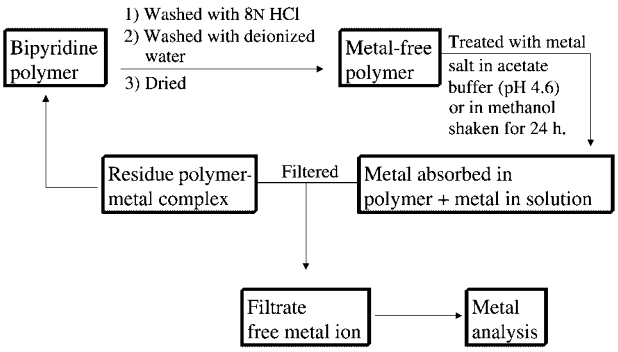


Figure 9. Sorption studies on polymers imprinted with metal complexes.[49]

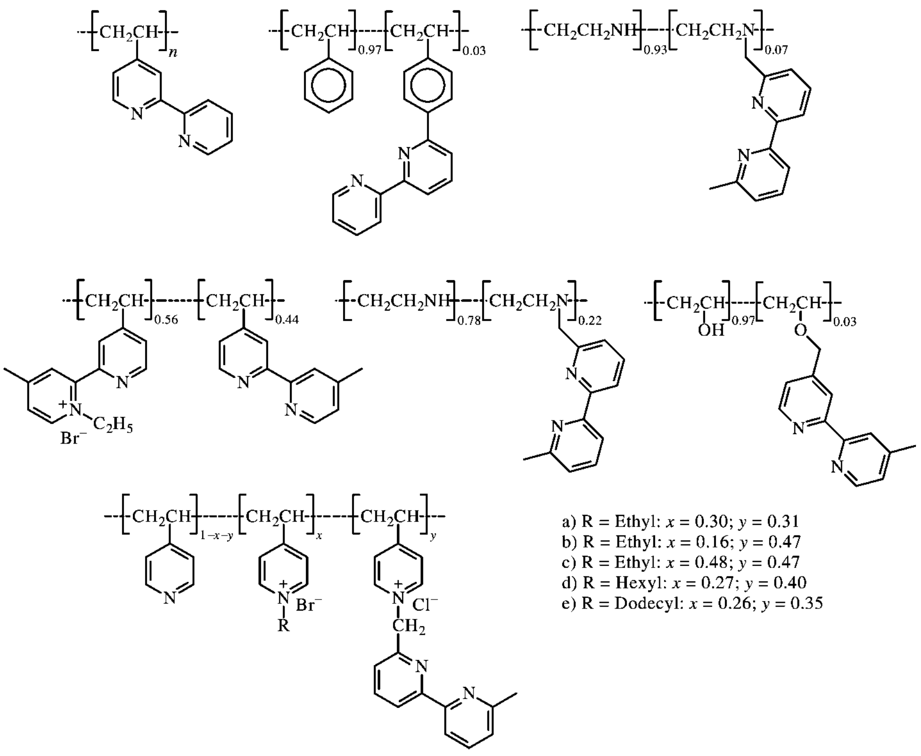


Figure 10. Polymers and their complexes as catalysts for the hydrolysis of organophoshate esters.[52, 53, 54]

In their search for polymeric catalysts for the hydrolysis of organophosphate esters, Pitt et al. used a different synthetic approach to 4-methyl-4′-vinylbipyridine.[52] Starting with commercially available 4,4′-dimethylbipyridine, they applied an *N*-oxide route via the monochloro- and the mono(methylenetriphenyl)phosphonium chloride to yield the monovinylene-functionalized bipyridine. Homopolymerization yielded a white non-cross-linked product that was soluble in organic solvents. Derivatization of commercially available poly(ethyleneimine), poly(vinyl alcohol), and poly(4-vinylpyridine) was also used to incorporate the bipyridine into the polymer side chain.[52, 53] A variety of polymeric amines was later investigated (Figure 10), and the catalytic activity of the polymer–metal complexes in the solvolysis of organophosphorus esters studied.[54] The highest activity was exhibited by copper(II) complexes of polymers containing the bipyridine group. At pH 7.6 and at a concentration of 3.7×10^{-3} mol L^{-1}, these catalysts reduced the half-life of diisopropyl fluorophosphate from 800 to 9 min.

Meyer et al. synthesized a series of redox-active [Ru(bpy)$_3$] polymers containing chromophores absorbing light in the visible region or organic energy transfer reagents (derivatized anthracenes).[55] They used the nucleophilic displacement of chloro substituents from poly(*m*(*p*)-(chloromethyl)styrene-*stat*-styrene) with alkoxide or carboxylate nucleophiles, under concomitant formation of amide and ether linkages (Figure 11). In the case of pendant bipyridine complexes, the corresponding unsymmetrically functionalized tris(bipyridine)ruthenium(II) complex was used as a nucleophile. In later work, tris(bipyridine)ruthenium(II) complexes and tris(bipyridine)osmium(II) complexes were attached to a polystyrene backbone. The type and length of the linkage as well as the molar ratios of the polystyrene and the pendant complexes were varied. A large difference in the ability of the ether and amide linker to promote intrastrand energy transfer was detected.[56–61] The electrogenerated chemiluminescence of these polymers in SiO$_2$ sol–gel/polymer composites was later studied.[62, 63] The sols were spin-coated onto an indium-tin-oxide (ITO) electrode and studied spectroscopically. While similar MLCT absorption spectra were detected (λ_{max} = 458 nm) in solution, the emission spectra of dry films were blue-shifted compared to those obtained in water or ethanol. The lifetime of the emissions in solution and film varies between 294 and 648 ns.

A partially cross-linked polymer based on poly(*N*-vinylcarbazole vinyl alcohol) with bipyridineruthenium luminophores was reported by Farah and Pietro in 1999 as a new material for electroluminescence.[64] Poly(*N*-vinylcarbazole vinyl alcohol) was cross-linked in a post-polymer modification by reaction with butyllithium and 5,5′-dibromomethylbipyridine. The resulting moiety was treated with bis(bipyridine)-ruthenium to obtain the corresponding polymer–ion complex shown in Figure 12. An investigation of the thermal and photochemical behavior demonstrated that the material was thermally stable up to 300 °C and exhibited emitted light at 590 nm upon radiation at the maximum absorption of 400 nm. The electroluminescence properties reported of poly(phenylenevinylene) with pendant bipyridine- or terpyridineruthenium complexes was reported by Chan and Wong (see Figure 57, Section 3.3).[65]

Newkome and Yoneda prepared homopolymers from 5-vinyl-6,6′-dimethylbipyridine,[66] a monomer not commonly used (Figure 13), and copolymers of the corresponding acrylate-functionalized bipyridine with styrene.[67] The polymers were treated with metal ions and the resulting complexes characterized by NMR and IR spectroscopy. The polymeric Pd^{II} complexes were later shown to be effective in the

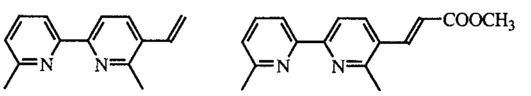


Figure 13. Unusual monomers prepared by Newkome and Yoneda.[66, 67]

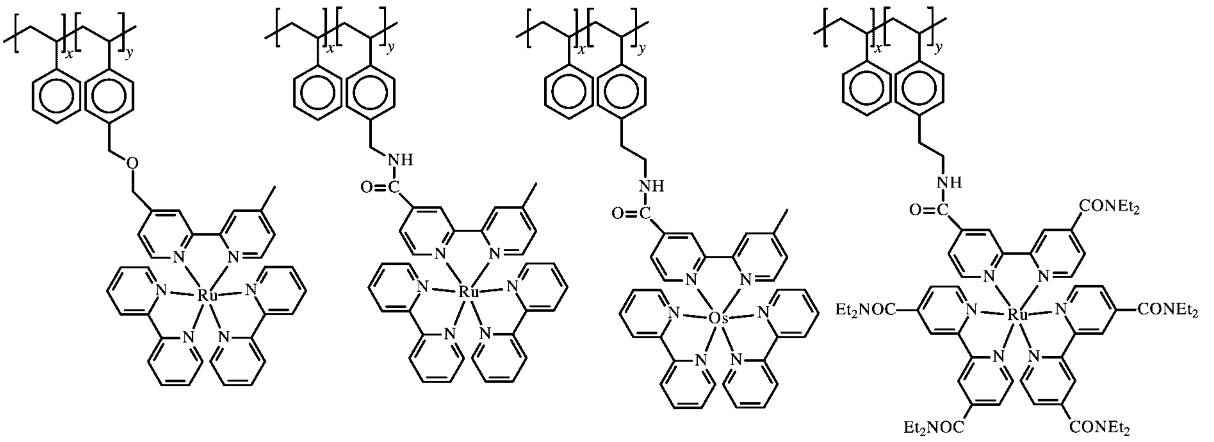


Figure 11. Polystyrene-bearing pendant bipyridineruthenium or -osmium complexes for the study of energy transfer.[55, 56, 57–61]

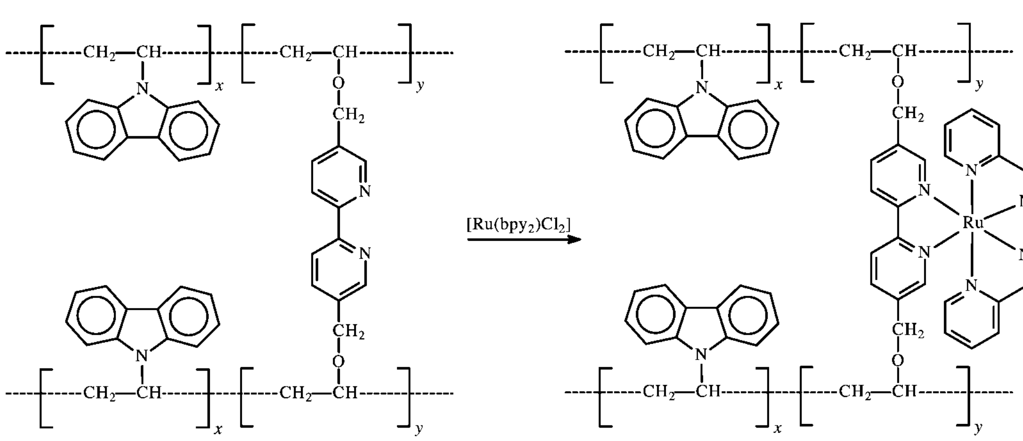


Figure 12. Synthesis of a new photoactive polymer–ruthenium complex.[64]

catalytic hydrogenation of simple olefins such as (*E*)-cinnamic acid.

Polystyrene-bound 2,2′-bipyridine–metal complexes were synthesized by Lei et al. and characterized by IR, X-ray, and photoelectric spectroscopy, by thermogravimetry, differential thermal analysis, inductively coupled plasma atomic emission spectrometry, and elemental analysis. The metal complexes were covalently attached to the polymer through the bipyridine and the free coordination sites on the metal ions were saturated with bipyridine, oxime, or phenanthroline units (Figure 14). The complexes were found to act as catalysts, in the absence of solvent, in the oxidation of alkyl benzenes and cyclohexene in the presence of molecular oxygen. Reaction rates of 3.57×10^4 to 3.83×10^5 $\mathrm{mL\,min^{-1}mol^{-1}}$ and a selectivity of oxidation to the ketone and alcohol ranging from 79 to 100 % were detected. The alcohol/ketone molar ratio of the products can be adjusted by employing additives or by varying the pH value of the reaction.[68–72]

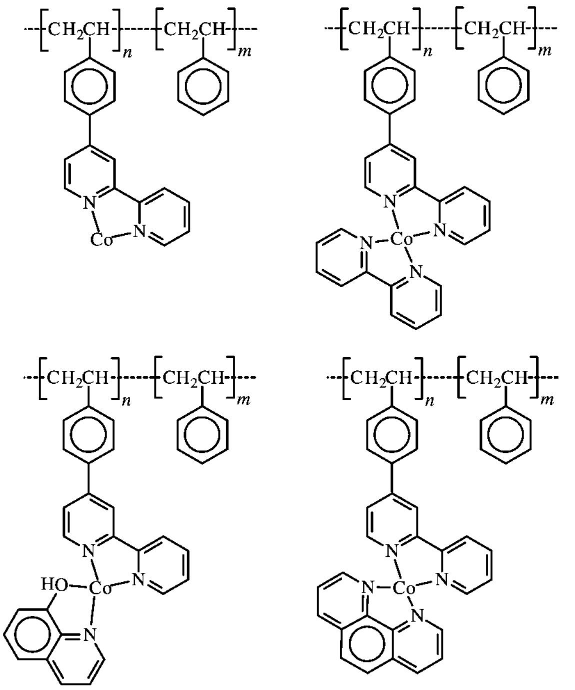


Figure 14. Polymeric catalysts prepared by Lei et al. for the oxidation of cyclic alkenes.[68]

A polymer-bound palladium catalyst for the synthesis of acetylene-terminated resins has been synthesized by Trumbo and Marvel from palladium diacetate and single-crystalline polyethylene containing pendant bipyridine units.[73] However, the authors found that the synthesized materials were unsuitable as supported catalysts for the planned reaction because of leaching, nonrecycability, and low yields.

The preparation of a series of copolymers of 2-hydroxyethyl methacrylate and 4-vinylpyridine or 4-methyl-4′-vinylbipyridine was reported by Miller and Lewis.[74–78] The addition of a solution of $FeSO_4$ or $CuCl_2$ to such polymers led to the formation of a hydrogel of cross-linked polymers. The mechanism and kinetics of the formation and the influence of the metal ions were also studied. Chujo et al. also published results on the formation of hydrogels from polyoxazoline-containing pendant bipyridine units.[79, 80] The addition of Co^{III} and Fe^{II} ions gave rise to noncovalent cross-linking and a swelling of the polymer. The Fe^{II}-containing gel was stable for several days at ambient temperature, but dissolved in hot water within 30 min. The stability of the Co^{III}-containing gel was lower than that of a Ni^{II}-containg gel, but higher than that of a Fe^{II}-containing gel. After reduction of the Co^{III} ions to Co^{II}, the polymer–ion complex was too labile to be handled as a hydrogel in water (Figure 15).

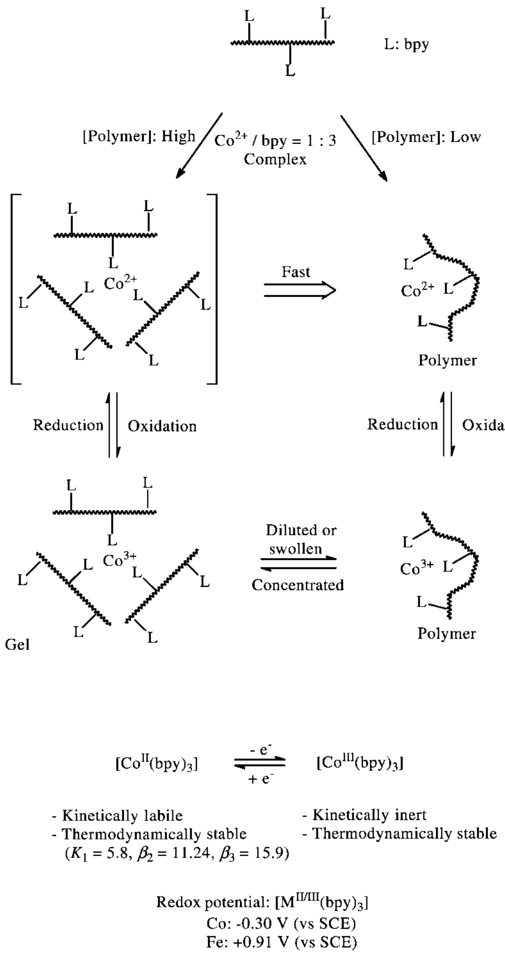


Figure 15. A thermally as well as oxidatively reversible hydrogel designed by Chujo et al.[79, 80]

Stimuli-responsive polymer gels as novel materials with sensor, actuator, and processor functions were investigated by Yoshida et al.[81–83] They copolymerized (Figure 16) the temperature-responsive *N*-isopropylacrylamide with bis(bipyridine)(4-methyl-4′-vinylbipyridine)ruthenium(II). Immersing the system in a Ce^{IV}/Ce^{III} solution induced the oscillatory Belousov–Zhabotinsky reaction,[84] and the gel swelled and deswelled periodically at a constant temperature without external stimuli. Depending on the composition of the environment, the chemical energy is transduced into mechanical energy and vice versa to drive the oscillation with a period of about 5 min.

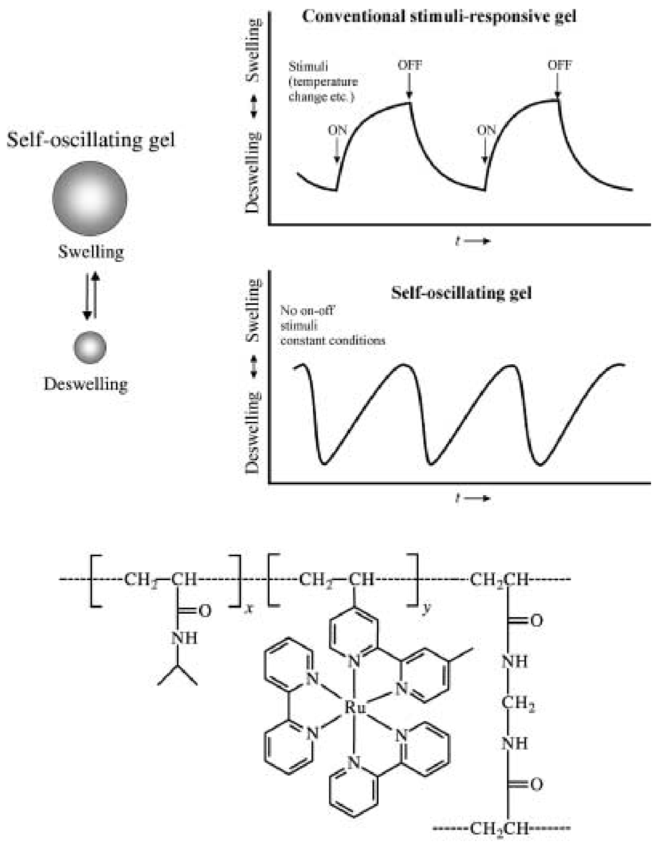


Figure 16. Self-oscillating gels based on *N*-isopropylacrylamide and copolymerized bipyridineruthenium complexes.[81]

Using a similar material, the tris(bipyridine)ruthenium(II) complex of *N*-isopropylacrylamide-*co*-(2-(4-(4′-methylbipyridyl))ethylacrylate), Miyashita et al. studied the electron-transfer quenching of the complex by methyl viologen as a function of temperature.[85] They determined the rate constant to be four to five times higher in the globular state than in the coil state. This result is in contrast to a similar experiment with a pyrene-labeled probe. This could mean that in the globular state the hydrophilic ruthenium complexes are placed at the interface of the hydrophobic polymer matrix and therefore are more easily accessible for the methyl viologen quencher (Figure 17). Later Miyashita and co-workers formed Langmuir–Blodgett films of these materials and investigated the photoelectrochemical response of a monolayer prepared on ITO.[86–89] A typical anodic photocurrent of 20 nA was determined upon irradiation of the film in the presence of an electron donator.

Bartsch et al. recently described 26 chelating copolymers for heavy-metal-ion sorption.[90] The copolymers were prepared by free-radical copolymerization of chelating monomers, such as 4-methyl-4′-vinylbipyridine, 2-vinylpyridine, or 4-vinylpyridine, with a dimethacrylate cross-linker (Figure 18). The bipyridine-containing polymers were shown to exhibit very efficient metal-ion sorption and were highly selective for Cu^{II} over Co^{II} and Ni^{II} ions and for Hg^{II} over Cd^{II} ions.

In 1995, Antonietti et al. presented microlatex dispersions with a surface of approximately 120 m^2 per gram of polymer

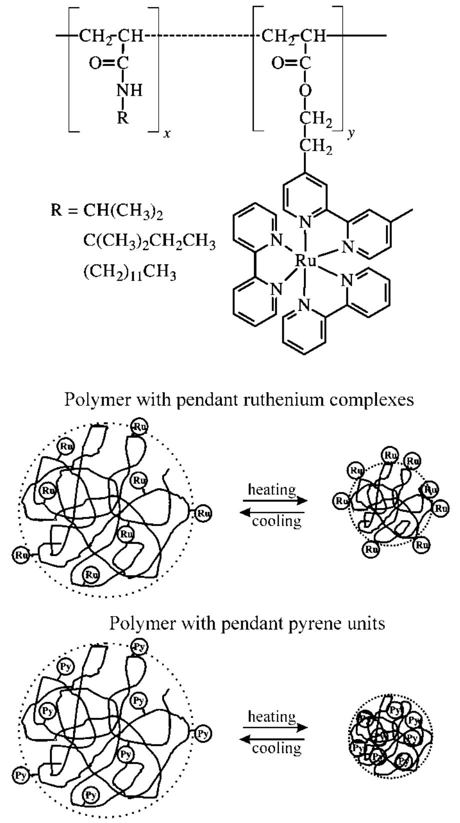


Figure 17. Top: A thermoresponsive polymer with pendant ruthenium complexes; bottom: in the globular state the hydrophilic ruthenium complexes are placed at the surface of the pyrene units within the polymer matrix.[85–88]

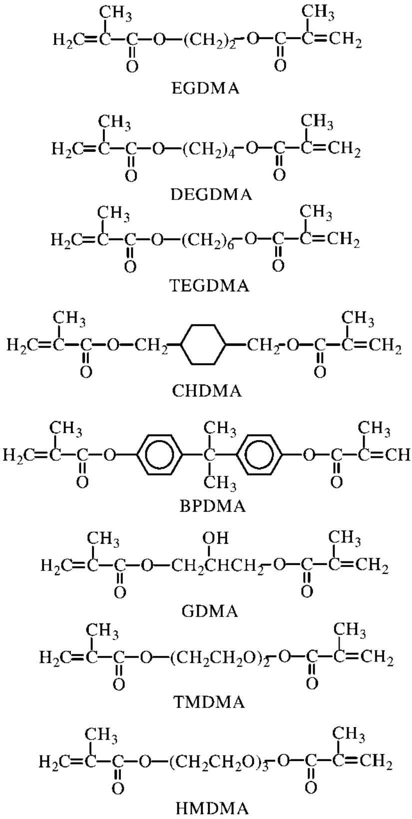


Figure 18. The different dimethacrylate cross-linking units for the preparation of chelating monomers for metal sorption.[90]

functionalized with bipyridine.[91] The polymers were synthesized by radical copolymerization of styrene and 10% (w/w) of 6′-methylbipyrid-6-ylmethyl methacrylate or 4-(6′-methylbipyrid-6-ylmethoxy)butyl methacrylate (Figure 19) and a cross-linking unit. Complexation experiments with transition-metal ions revealed that most of the bipyridine units were located at the latex surface and were accessible in the binding process.

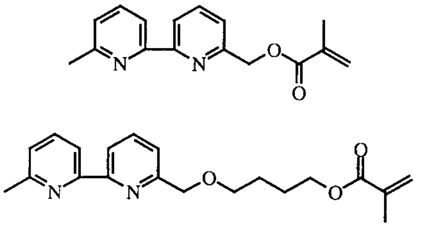


Figure 19. Methacrylate-functionalized bipyridine ligands for the preparation of metal-complexing microlatex dispersions.[91]

A system completely different to those shown above was presented by Lindsell et al. in 1999,[92] in which they investigated polydiacetylenes with bipyridine ligands in the side chain as systems with nonlinear optical properties (Figure 20).

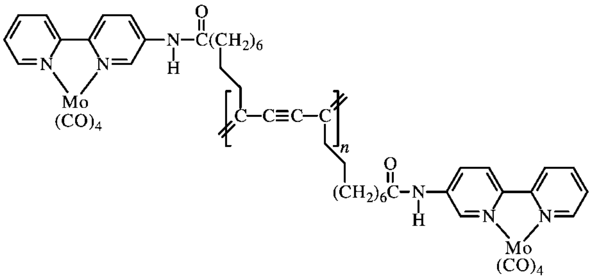


Figure 20. Functionalized poly(diacetylenes) for nonlinear optics.[92]

The monomers were synthesized by reaction of carboxy-functionalized 1,3-diynes and 5-aminobipyridine to obtain the corresponding amides. Polymerization was achieved by UV or γ irradiation at room temperature, and resulted in an insoluble material. The addition of metal ions resulted in the corresponding polymeric ruthenium(II) and molybdenum(0) complexes becoming soluble. Their linear absorption coefficients were determined to be 25.8 cm^{-1} for the Ru^{II}-complex and 33.2 cm^{-1} for the Mo^0-containing polymer. Their nonlinear absorption coefficients were determined to be -6.5 and -8.5 $cm\,GW^{-1}$, respectively.

2.3. Polymers with Bipyridine Units in the Polymer Backbone

Yamamoto et al. published several papers on polymers with bipyridines in the polymer backbone.[93–104] In earlier approaches, 5,5′-dihalogeno-substituted bipyridines were reacted in the presence of nickel(0) catalysts, which resulted in rather low-molecular-weight polymers ($\bar{M}_w = 3800$; degree of polymerization (DP) = 21) that were only partially soluble in formic acid.[93–95] In contrast to the uncomplexed polymer, metal-containing oligomers ($\bar{M}_w = 1500$) were demonstrated to be soluble in water.[102] The soluble polymeric platinum or ruthenium complexes can act as photocatalysts for H_2 evolution from aqueous media.[101, 102] The polymeric complexes can also transfer the photoactivated energy to other molecular parts of the systems and thus cause emission of light from other parts of the molecules (Figure 21, top).[99] Evidence for this energy transfer was demonstrated by the absorption at 350 nm, which was assigned to the poly(bipyridine) unit, and the fluorescence emission at 640 nm, which was assigned to the Ru^{II} complex. The degree of polymerization was increased to 65 ($\bar{M}_w = 21000$) by changing to 6,6′-dihexyl-substituted bipyridines; these polymers remained soluble.[97, 98] The steric effects of the alkyl groups resulted in the π conjugation being shortened in these systems.

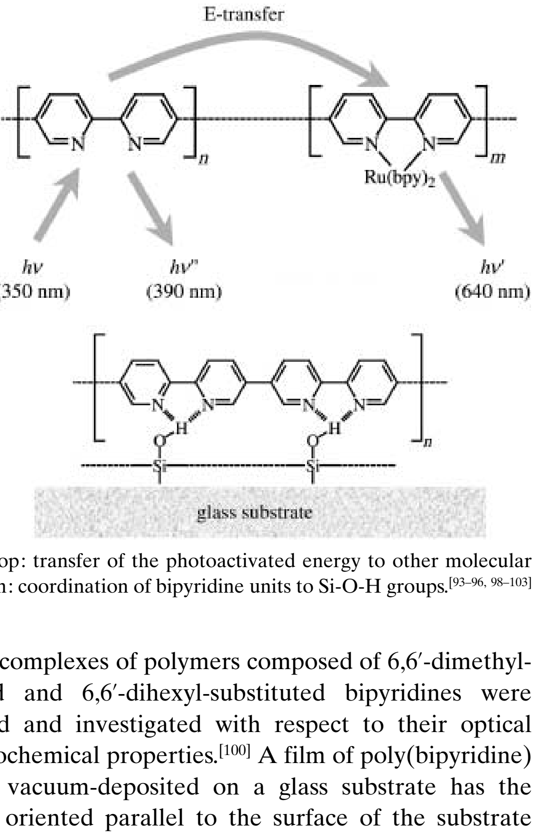


Figure 21. Top: transfer of the photoactivated energy to other molecular parts; bottom: coordination of bipyridine units to Si-O-H groups.[93–96, 98–103]

Copper complexes of polymers composed of 6,6′-dimethyl-substituted and 6,6′-dihexyl-substituted bipyridines were synthesized and investigated with respect to their optical and electrochemical properties.[100] A film of poly(bipyridine) molecules vacuum-deposited on a glass substrate has the molecules oriented parallel to the surface of the substrate (Figure 21, bottom). The coordination of poly(bipyridine) to the substrate is proposed to explain such an orientation.[98]

In 1985, Sassoon described a two-electrolyte system for energy storage based on tris(bipyridine)ruthenium compounds and a *N,N,N,N*-tetraalkyl-*p*-phenylenediamine derivative bound covalently to a poly(3,3-ionene) polyelectrolyte (Figure 22).[105] An inhibition of more than five orders of magnitude in the photochemical properties of the system were found relative to the reverse electron-transfer reaction between $[Ru(bpy)_3]$ and the radical cation of *N,N,N,N*-tetraalkyl-*p*-phenylenediamine.

In 1997, Wasielewski and Wang published a sophisticated approach to metal-ion-sensitive polymers,[106] in which they chose a partially conjugated polymeric system consisting of oligo(*p*-phenylenevinylene) segments that were covalently

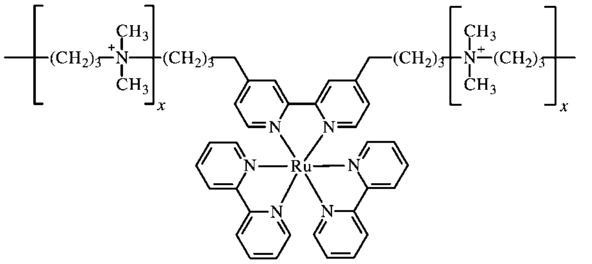


Figure 22. Covalent binding of a photosensitizer to a polyelectrolyte by Sassoon.[105]

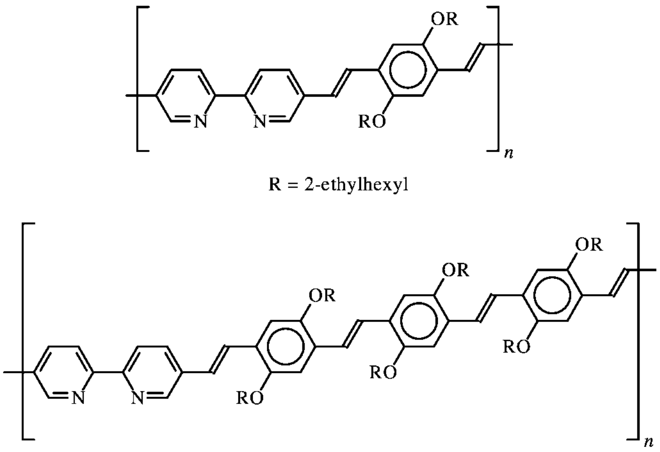


Figure 23. Partially conjugated ion-sensitive polymers.[106]

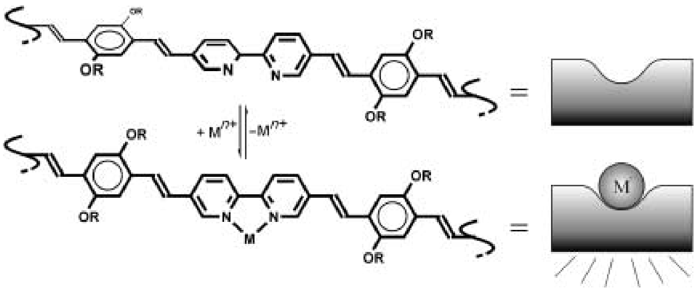


Figure 24. Chelating a metal ion forces the bipyridine group from a twisted conformation into a planar one and enables full conjugation of the polymer.[106]

connected to bipyridines at their 5,5′-positions by a Wittig-type reaction. As shown in Figure 23, two polymers with different segment ratios were synthesized. The transoid conformation of the free bipyridines means there is a dihedral angle of approximately 20° between the pyridine planes. The corresponding metal complexes have been formed, and the optical behavior of the free polymer and the polymer–ion complex has been compared. Since the twisted conformation is forced into a planar one upon metal complexation and the partially conjugated polymer is therefore transformed into a fully conjugated polymer, different physical properties are obtained (Figure 24). The addition of Pd^{II} ions to the polymer shown in Figure 23 (top) shifts the absorption maximum of the uncomplexed polymer from 455 to 564 nm. Different absorption maxima were obtained with different metal ions, with the shift ranging from 38 to 112 nm. Chen et al. studied the effects of π conjugation on the photophysics and excitation dynamics of these polymers.[107] Relative to the homopolymers, they demonstrated blue shifts in their absorption and emission spectra, spectral diffusion in stimulated emission, and enhancement in their photoluminescence quantum yields and lifetimes. The ionochromic effects and structures of the metalated polymers were recently published.[108]

Yu et al. utilized Heck-coupling reactions to synthesize photorefractive copolymers based on *p*-phenylenevinylene and tris(bipyridine)ruthenium or tris(bipyridine)osmium complexes for nonlinear optics.[109, 110] A variety of polymers with slightly different substituents to enhance the solubility were reported. While most polymers were synthesized by Heck coupling of iodo-substituted tris(bipyridine)ruthenium complexes with *p*-phenylenevinylene or other iodo-substituted co-monomers (Figure 25), there has been one approach utilizing the Horner–Wadsworth–Emmons reaction of free bipyridine ligands and metal complexation after polymerization (Figure 26). Klemm et al. also used the Heck-coupling procedure for the preparation of conjugated organic polymers.[111, 112]

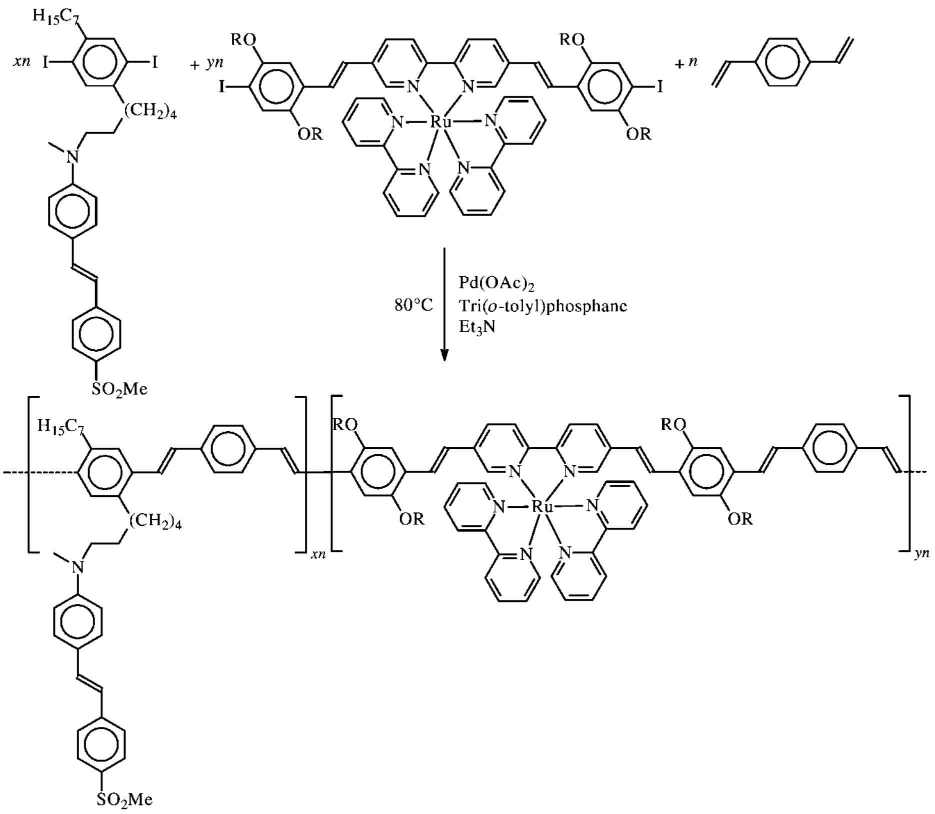


Figure 25. Heck coupling of alkenes with aryl iodides.[110]

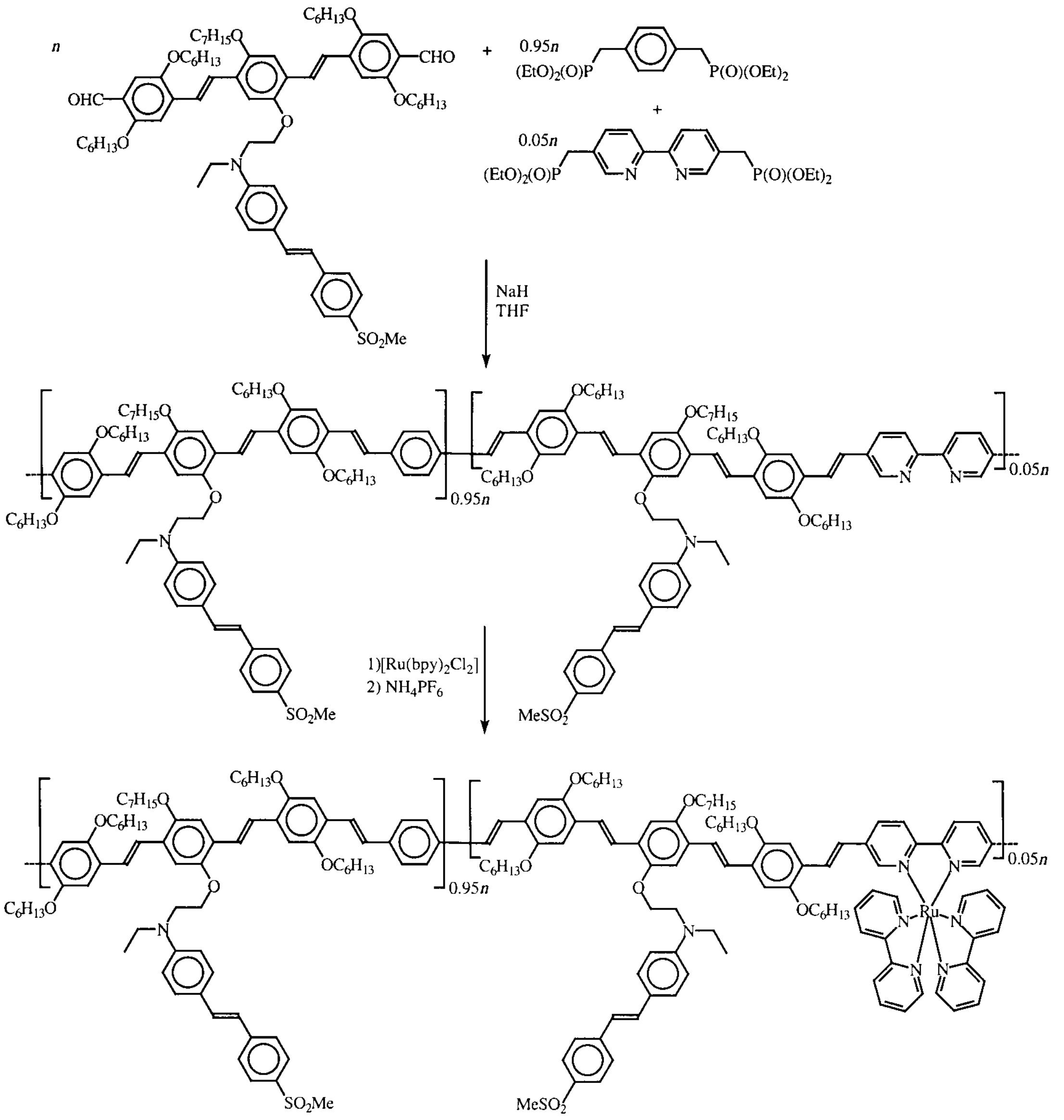


Figure 26. Horner–Wadsworth–Emmons reaction for the synthesis of photorefractive polymers.[110]

The reaction of 5,5′-dibromobipyridine and substituted phenyldiacetylenes provided conjugated polymers with a rigid backbone and molecular weights up to 23000 $\mathrm{g\,mol^{-1}}$ (Figure 27 a). The polymers were characterized by NMR and UV/Vis spectroscopy, gel permeation chromatography (GPC), and vapor-pressure osmometry. Fluorescence quantum yields ϕ_{fl} between 71 and 96 % make these new compounds potential candidates for light-emitting diode (LED) or laser-dye applications. The corresponding polymeric metal complexes have not yet been prepared. Conjugated polymers comprising the arylene–ethylene architecture have also been published by Schanze et al. (Figure 27 b).[113–115] Similar to the system described by Wasielewski and Wang (Figure 23),[106] the transoid bipyridine was forced into a cisoid conformation upon complexation and, therefore, the conjugation in the polymer was extended. For this purpose, instead of chelating the polymer after polymerization, bipyridinerhenium(I) complexes were polymerized. Spectroscopic studies revealed fluorescence at 435 nm (2.85 eV) in all the polymers at 298 K, with the fluorescence being quenched with increased molar fractions of $\mathrm{Re^{II}}$ in the polymer.

In 1986, Evers and Moore were the first to prepare bipyridine-containing poly(benzobisoxazole)s and poly(benzobisthiazole)s[116] when they copolymerized bipyridine-4,4′-dicarboxylic acid chloride with terephthalic acid and 4,6-diamino-1,3-benzenediol dihydrochloride or 2,5-diamino-1,4-benzenedithol. The polymers were essentially unaffected at 316 °C and displayed thermo-oxidative stability for 200 h. Chan et al. later reported the synthesis and physical properties of a series of poly(benzobisoxazole)s and poly(benzobisthiazole)s containing bipyridine derivatives.[117, 118] These polymers were synthesized by polycondensation of bipyridine-4,4′-dicarboxylic acid or bipyridine-5,5′-dicarboxylic acid and diaminobenzenediols in poly(phosphoric acid) (Figure 28). The polymers exhibited thermal stabilities up to 650 °C in a nitrogen atmosphere and up to 590 °C in air. Polymers containing bipyridine-5,5′-dicarboxylic acid demonstrated a lyotropic liquid-crystalline phase in methanesulfonic acid;

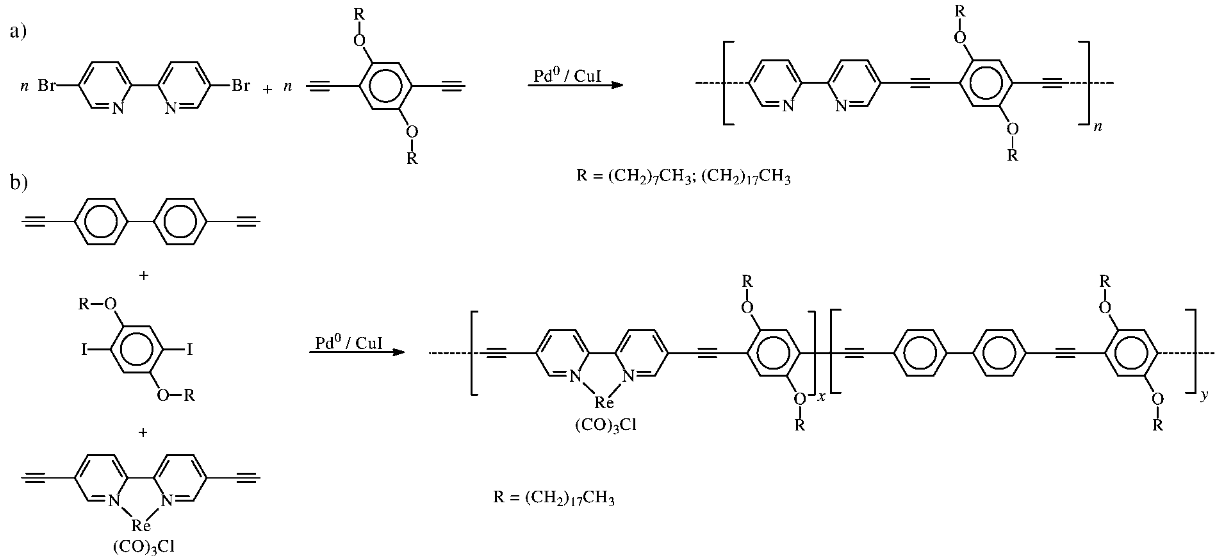


Figure 27. Conjugated polymers based on bipyridine and aryl diacetylene a) ref. [111, 112]; b) ref. [113].

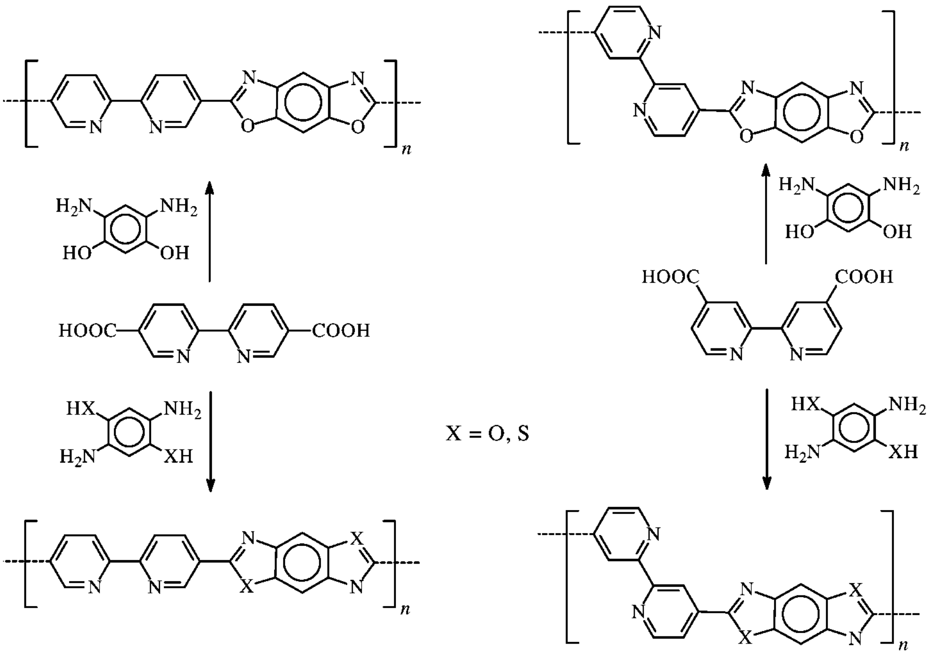


Figure 28. Poly(benzobisoxazole)s and poly(benzobisthiazole)s containing bipyridine units in the backbone.[117]

however, the polymers containing bipyridine-4,4′-dicarboxylic acid did not demonstrate any anisotropy. The formation of polymeric ruthenium complexes increases the mobility of the charge carriers by two orders of magnitude to $10^{-5}\,cm^2V^{-1}s^{-1}$.

Rigid-rod benzobisazole polymers as well as poly(benzobisthiazole)s and poly(benzobisoxazole)s with main-chain bipyridine-5,5′-diyl units were reported by Tan et al. in 1999 (Figure 29).[119] The polymers were doped with $AgNO_3$ to enhance the conductivity from 10^{-10}–$10^{-8}\,S\,cm^{-1}$ to 10^{-5}–$10^{-4}\,S\,cm^{-1}$. A conductivity of 25–42 S cm^{-1} resulted when Ag^+ was reduced to Ag^0 by $NaBH_4$.

In more recent work, Chan et al. published a broad range of bipyridine-based polyamides (Figure 30 a) and polyesters (Figure 30 b).[120, 121] Polyamides were synthesized by Yamazaki's method using pyridine and triphenyl

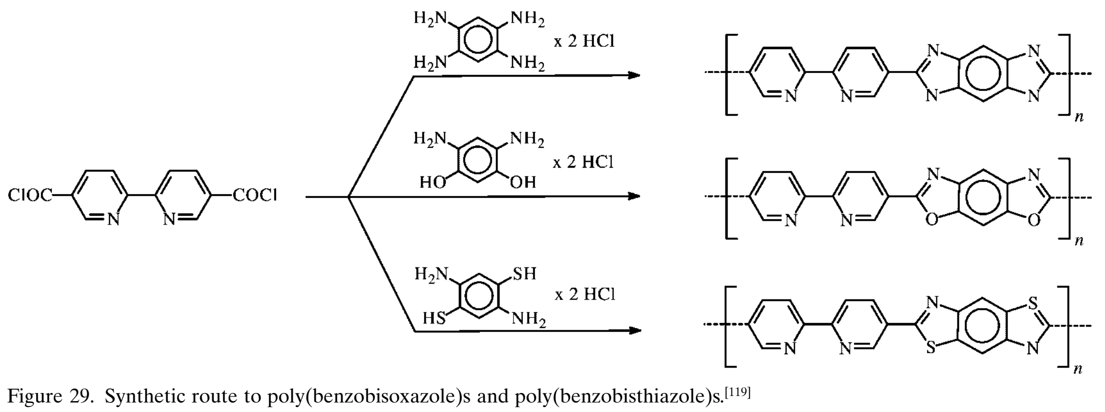
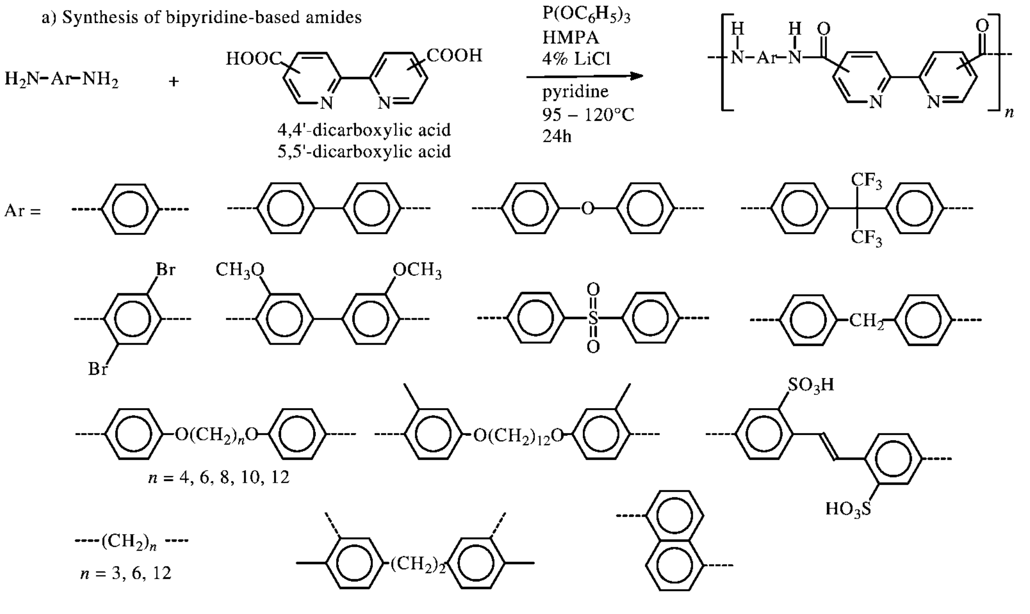


Figure 29. Synthetic route to poly(benzobisoxazole)s and poly(benzobisthiazole)s.[119]

a) Synthesis of bipyridine-based amides



b) Synthesis of bipyridine-based polyesters

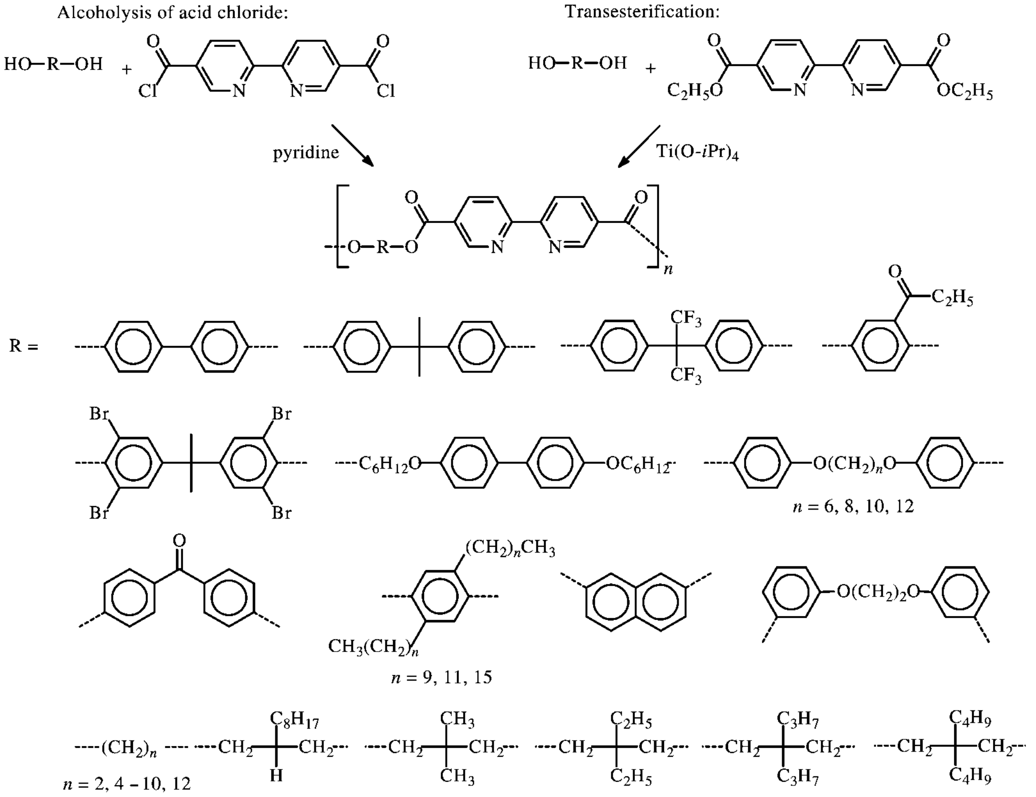


Figure 30. Polyamides (a) and polyesters (b) based on bipyridine.[121]

phosphite. The resulting polymers based on bipyridine-5,5′-dicarboxylic acid demonstrated a higher viscosity and decomposition temperature (300–500 °C) than polymers based on bipyridine-4,4′-dicarboxylic acid. Polyesters were synthesized by either alcoholysis of acid chlorides or transesterification. The decomposition temperatures for the polyesters were demonstrated to be in a narrower range, namely 320–440 °C. The molecular weight of the polymers could not be determined by GPC measurements because of their insolubility in common solvents. Static light scattering techniques were, therefore, applied and molecular weight values of 20000–40000 g mol^{-1} were determined for the polyamides. The polymers were treated with bis(bipyridine)ruthenium complexes to incorporate metal ions.

Thermotropic liquid-crystalline polyesters with the bipyridine unit acting as a mesogene were synthesized by Hanabusa et al. in 1989 (Figure 31).[122] Polyesters bearing an alkyl chain as a co-component are smectic in the absence or at low

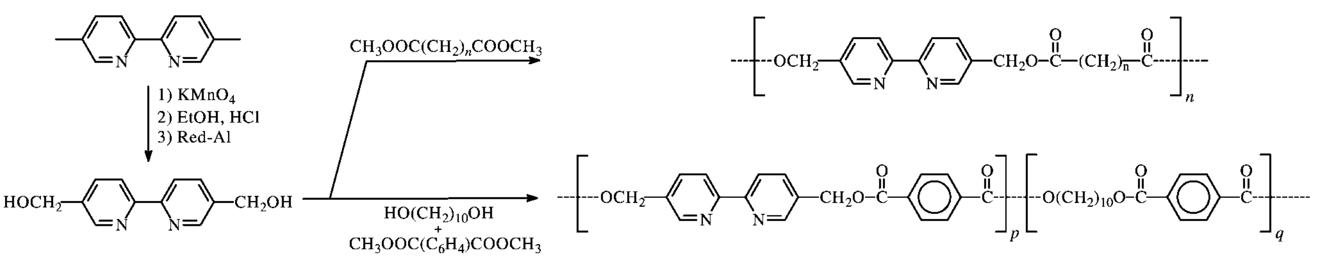


Figure 31. Liquid-crystalline polyesters showing thermotropic behavior after the addition of several molar equivalents of metal ions ($FeCl_2$ or $CuCl_2$).[122]

concentrations of metal ions. A nematic mesophase was observed in the case of the aromatic polyesters. Two endothermic transitions at 114 and 135 °C, respectively, arising from the transition from the crystalline to the liquid-crystalline and finally to the isotropic state were observed regardless of the kind and amount of metal ions present. The structural properties of a polyester–Cu^{II} complex were examined by ESR spectroscopy. Several years later, Rubner et al. described the synthesis of a polyester similar to that synthesized by Hanabusa et al.[122] by utilizing a modified Schotten–Baumann reaction of 4,4′-bis(hydroxymethyl)bipyridine and dodecanedioyl dichloride in THF.[123, 124] However, since the solubility of the resulting polymer was poor, they treated bis(hydroxymethyl)bipyridine with $[Ru(bpy)_2Cl_2]$ and polymerized the resulting Ru complex with dodecanedioyl dichloride to obtain a polymer with an average molecular weight of about 5500 $g\,mol^{-1}$. The polymer became soluble in acetone by using PF_6^- counterions. In contrast, when the counterions were changed to Cl^-, the new polymer was soluble only in polar solvents such as water or methanol. Light-emitting devices were produced from these materials by utilizing either a spin-coating technique or a layer-by-layer self-assembly. The spin-coated devices produced maximum luminance levels of 250–300 $cd\,m^{-2}$ with an external quantum efficiency of 0.2 % photons per electron. Devices based on sequentially adsorbed layers of the polyester and poly(acrylic acid) exhibited a maximum light output of 40–50 $cd\,m^{-2}$ and external quantum efficiency of 1–3 % photons per electron.[123, 124]

Polyamides and polyureas with acyclic and cyclic bipyridyldiamino structures in the polymer backbone were described by Pappalardo et al. in 1987.[125, 126] While the polymer containing the acyclic bipyridine moiety formed stable metal complexes with Co^{II}, Cu^{II}, or Ni^{II} ions, the cyclic structure exhibits a special affinity towards Cu^{II} ions (Figure 32). The polymers were characterized by NMR and IR spectroscopy and their thermal behavior was studied. The polyamides were stable at temperatures above 400 °C, while the polyureas decomposed between 300 and 400 °C. The first bipyridine-containing polyureas were reported by Zhang and Neckers in 1983.[127–129] The polymers were prepared from 4,4′-diaminobipyridine and toluenediisocyanate. The metal-complexing abilities of the polymers, in particular with cobalt, palladium, and vanadium ions, were investigated with special attention to the catalytic activity in the hydrogenation and epoxidation of olefins and in the aldol condensation. In addition to the soluble linear polymers, insoluble cross-linked moieties were prepared. In 1985, Neckers et al. reported on polyamides and their Pd^0 and Rh^{III} complexes.[130, 131]

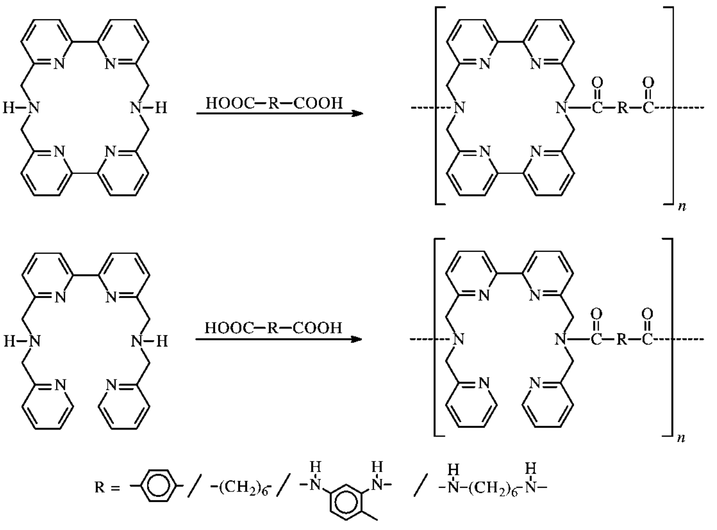


Figure 32. Polyamides and polyureas with cyclic and acyclic bis(bipyridyl) structures synthesized by Pappalardo et al.[125, 126]

Polyimides consisting of 5,5′-diamino-bipyridine derivatives and aromatic tetracarboxylic acid anhydrides that were designed to be more heat-resistant, were described by Kurita and Williams in 1973.[132–134] They also synthesized similar poly(amidoimide)s. In most cases, the pyridine units of the bipyridine derivatives were separated by a heteroatom or a functional group X (X = S, NH, or SO_2), but some were also linked together directly (Figure 33). Yang and co-workers later described polyimides consisting exclusively of 2,2′-bipyridine (Figure 33, top, X = –).[135] They treated 5,5′-diaminobipyridine with three different aromatic dianhydrides, heating then effected imidization to obtain fairly thermostable polymers, for example, only a 5 % weight loss occurred

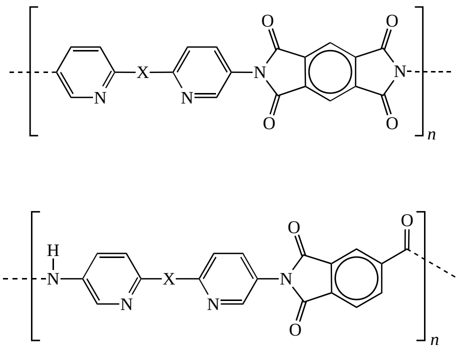


Figure 33. Polyimides and polyamideimides (X = –, S, SO, SO_2, NH) synthesized from 5,5′-diaminobipyridine derivatives.[132, 133]

in the range of 480–580 °C. The polymers were treated with several different transition-metal ions, and the catalytic activity of the polymeric complexes in the condensation of benzaldehyde with acetophenone was investigated. The degree of catalytic activity for different metal ions was demonstrated to be in the order $Zn^{II} > Co^{II} > Cu^{II}$ and the yield of 1,3-diphenyl-2-propen-1-one was in the range of 6–32 %. Recently, Chen et al. reported on novel polyimides (Figure 34) based on bipyridine.[136] In addition to the synthesis, the group investigated the influence of the coordination of malenonitriledithiolatenickel on the copolymers, in particular on their thermal stability. The polymers had elevated glass transitions in the range of 270–320 °C and decomposition temperatures ranging from 370–520 °C. Majumdar and Biswas published the reaction of pyromellitic dianhydride with unsubstituted bipyridine in 1991.[137, 138] In our mind, the presented structures are to be doubted and will not be considered any further.

In 1997, Kira and co-workers published the synthesis of poly(disilanylene-2,2′-bipyridine-5,5′-diyl) and poly(silylene-2,2′-bipyridine-5,5′-diyl) and their ruthenium complexes (Figure 35).[139] The polymeric ruthenium complexes underwent metal-to-ligand charge-transfer excitation which resulted in photoconductivity. A photocurrent with a maximum at 470 nm of approximately 1.8×10^{-13} A was measured in a sandwich-type cell with aluminum and ITO as the top and bottom electrodes, respectively, at 6 V. The optical properties of the polymeric metal complexes were studied two years later.[140] A noncovalent polymerization of bis(bipyridine)alkanes was carried out by Ching and Elliot in 1999.[141] The addition of iron and cobalt ions to spin-coated films of the monomers shown in Figure 36 resulted in highly cross-linked electroactive coordination polymers. Charge-transport measurements by chronoamperometry on thin films of the Fe^{II}-containing polymer in which the alkyl linker consists of 2, 4, and 6 methylene groups shows $D^{1/2}C$ values (D = charge-

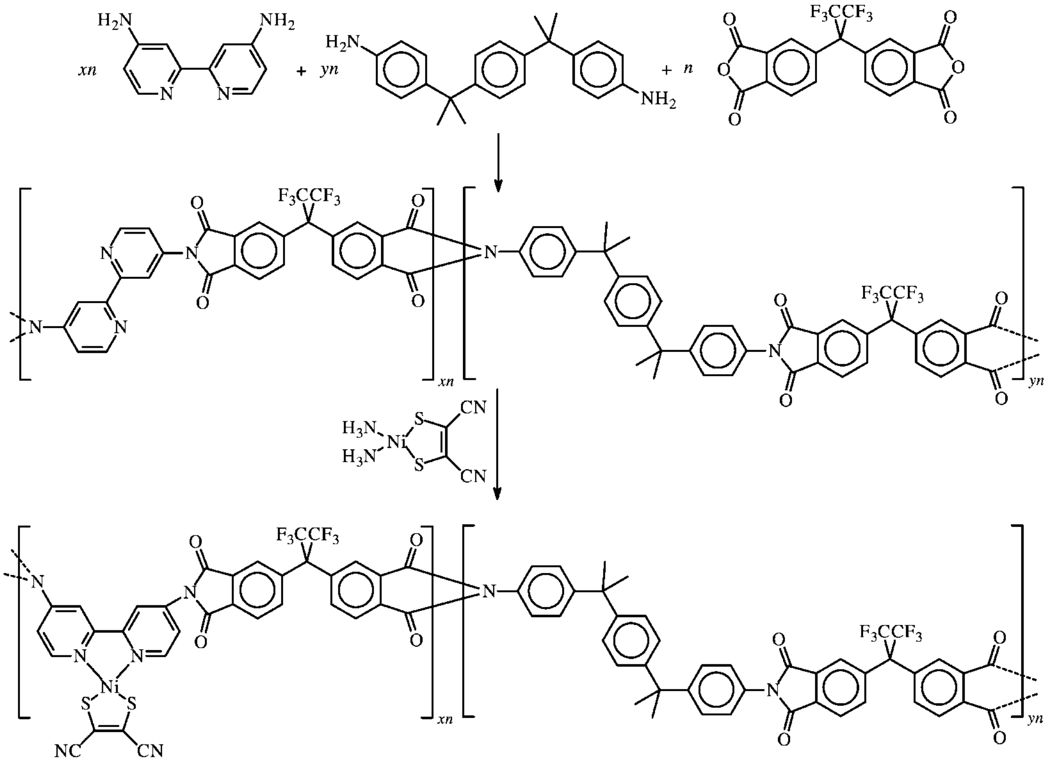


Figure 34. Copolymers based on polyimides with bipyridine units in the polymer backbone.[136]

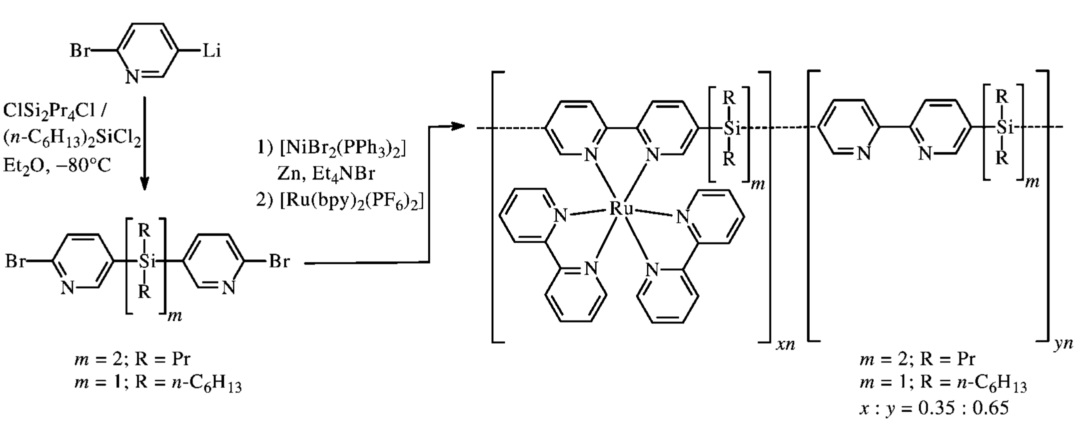


Figure 35. Synthesis of σ-π-alternating copolymers and their ruthenium complexes by Kira and co-workers.[139, 140]

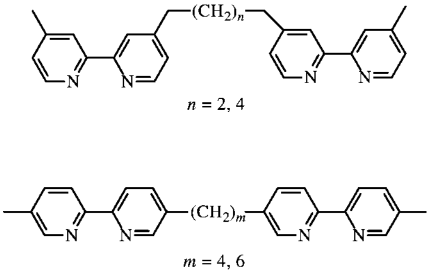


Figure 36. Coordinative polymer films were prepared by adding metal ions to the shown ligands.[141]

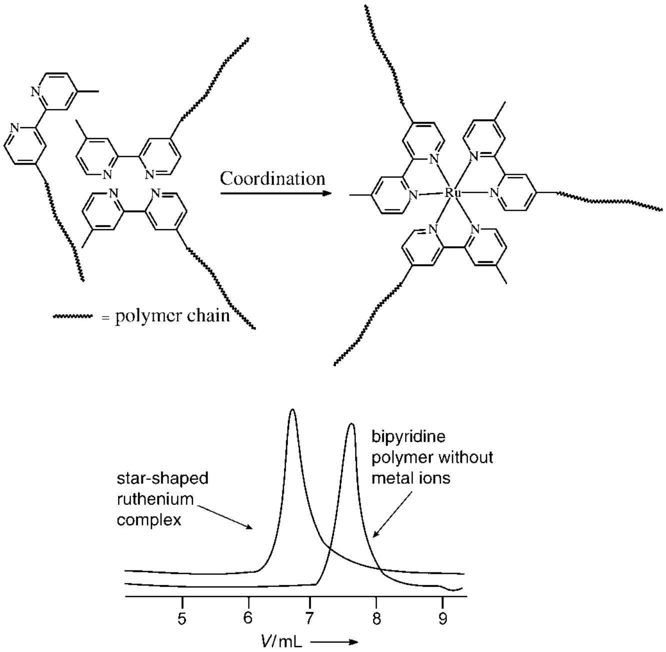


Figure 37. Top: Preparation of star-shaped polymers by the addition of metal ions to monofunctionalized bipyridine polymers; bottom: GPC analysis showed a significant shift in the molecular weight after complexation.[143, 145]

transfer diffusion coefficient; C = concentration of redox sites) ranging from 9.5×10^{-8} to 2.3×10^{-8} mol cm^{-2}s$^{-1/2}$ at 298 K and follow a trend of decreasing $D^{1/2}C$ values with increasing length of the alkyl chain. No such trend was observed for the analogous systems linked through the 5-position. Attempts to prepare polymer films with other metal ions such as Ni^{II}, Cu^{II}, or Ru^{II} failed.

A special case of polymers containing bipyridine units in the polymer backbone are molecules containing only one bipyridine unit. The addition of metal ions to that moiety results in star-shaped polymers. Different approaches to these structures have been reported in the literature. Murray and co-workers treated bipyridine-4,4′-dicarboxylic acid chloride with poly(ethylene oxide) monomethyl ester ($M_w = 350$) to reveal the substituted ligand 4,4′-di(poly(ethylene oxide) methyl ether)bipyridine.[142] The transport, ionic conductivity, and viscosity properties of the molten salt were studied after addition of cobalt perchlorate. For $LiClO_4$ (1.3 M), the average diffusive jump rate was about 3 s^{-1}, the average electron-hopping rate was about 2×10^4 s^{-1}, and the rate of short-range motions of the hard metal complex core within its soft polyether shell was determined to be about 10^5 s^{-1}.

Chujo et al. synthesized bipyridines substituted on just one side with poly(ethylenoxide)s or poly(propylenoxide)s (Figure 37)[143–145] by starting with 4,4′-dimethylbipyridine. Reaction with LDA and subsequent addition of an α-alkyl ether-ω-tosylate polymer yielded the desired polymer containing a single bipyridine unit. The addition of metal ions such as Ni^{II}, Co^{II}, or Ru^{III} yielded star-shaped structures, which were investigated by UV/Vis spectroscopy and GPC analysis. While the Ru complexes were stable against shearing forces under GPC conditions, the Ni^{II} and Co^{II} complexes dissociated. Following the current interest in metal clusters and colloids in the size range of 1–10 nm for catalytic use and as advanced materials in electronics (for example, as quantum dots), poly(ethylene oxide)-grafted palladium clusters were prepared and used in a first application.[145]

A completely different approach towards star-shaped polymers was established by the research groups of Fraser and Schubert.[146–155] They used metal complexes of halomethyl-substituted bipyridines as initiators for the living cationic polymerization of 2-oxazolines. The polymer growth starts from the metal complex and, depending on the substitution pattern of the complex, several different structural types are accessible (Figure 38). To obtain a higher order of structural diversity, not only 4,4′-bipyridines were utilised, but 5,5′- and 6,6′-functionalized bipyridines were used as well. In addition, the living character of the polymerization and the accessibility of suitable monomers, for example, 2-ethyloxazoline, 2-phenyloxazoline, and 2-undecyloxazoline, allow the preparation of amphiphilic block copolymers (Figure 39). Finally, depending on the choice of a suitable termination reagent, more functionalities can be introduced into the molecules. In the case shown in Figure 39, the oxidation of the Cu^{I} ion to Cu^{II} would switch from the star-shaped molecule to a linear system since Cu^{II} ions cannot form stable complexes with 6,6′-substituted bipyridines, but is chelated by terpyridines to form very stable complexes.

The principle of initiating polymerization by supramolecular metal complexes and ligands does not only work with oxazolines. In two independent papers, Schubert and Hochwinner as well as Wu and Fraser recently used 6,6′-substituted bipyridinecopper(I) complexes[156] and 4-mono- and 4,4′-disubstituted bipyridines[157] as initiators for the controlled radical polymerization of styrene (Figure 40). While we used the tris(4,4′-dimethylbipyridine)copper(II) complex as the catalyst for polymerization and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone as the solvent, Fraser's group used either 4,4′-bis(tridecyl)bipyridine or 1,1,4,7,10,10-hexamethyltriethylenetetramine and CuBr or CuCl as catalysts. Polymerization was carried out either in the bulk or in solution with anisole as the solvent. For a further extension of this method, the same research groups have recently used the so-called "co-initiator approach" with hydroxy-functionalized N-heterocyclic ligands as the co-initiator and aluminum alkoxides as efficient initiators for the ring-opening polymerization of ε-caprolactone and lactid acid (Figure 41).[158–161]

The formation of well-defined structures by self-assembly is the central theme of supramolecular chemistry. Polymers with

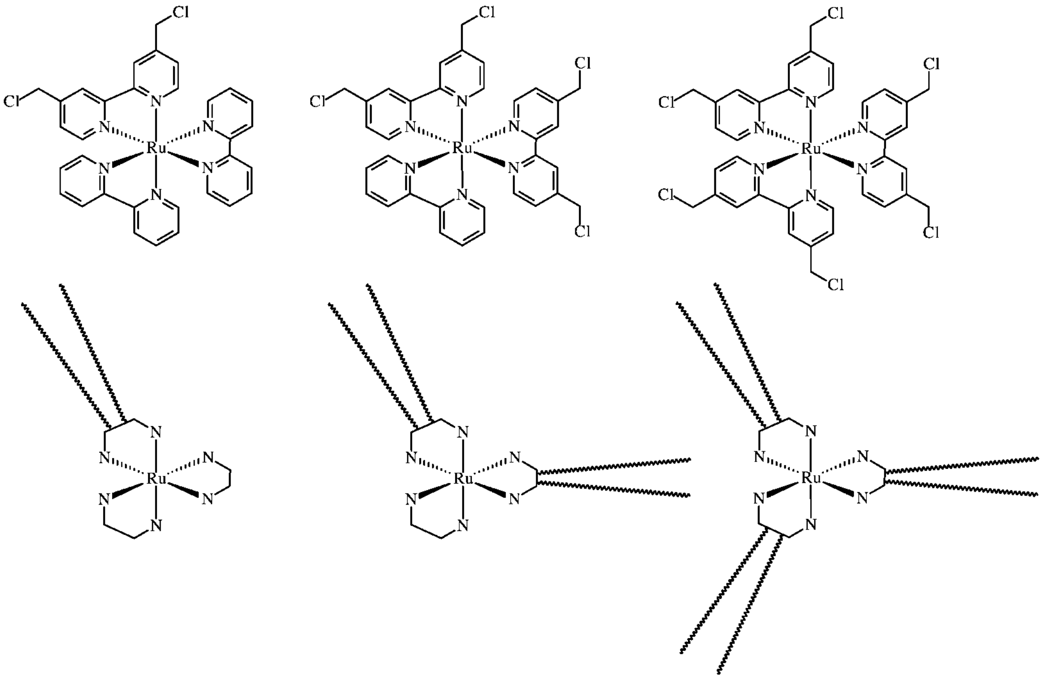


Figure 38. Different substitution patterns of the metal complex (upper row) give access to different structural types of star-shaped molecules (lower row).[155]

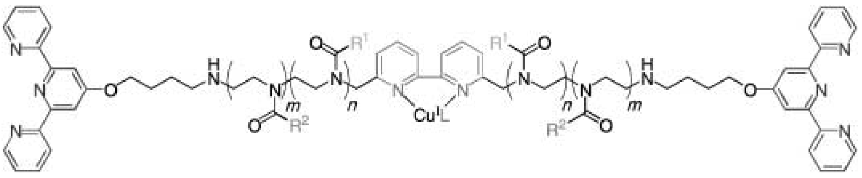


Figure 39. Amphiphilic macromolecule with two different metal-binding sites (R^1 = Et, R^2 = Ph).[153]

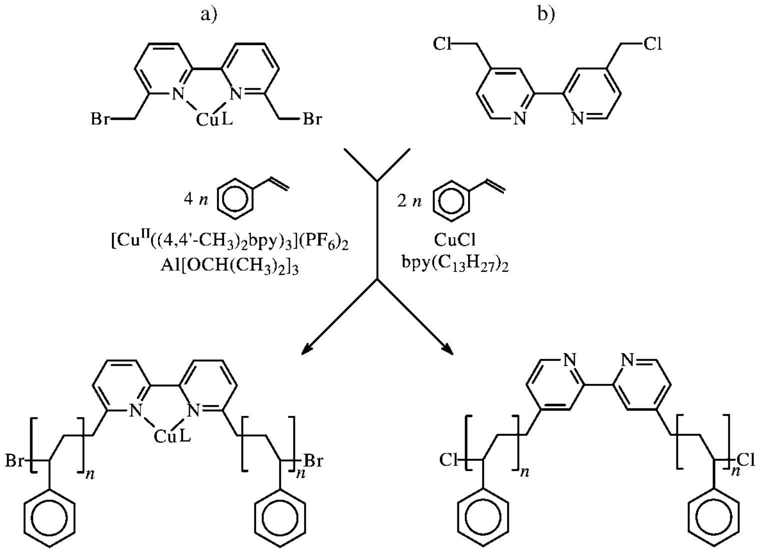


Figure 40. Synthesis of star-shaped polystyrene by using metallosupramolecular initiators and catalysts (a);[156] and a functionalized bipyridine for initiation and CuCl/bipyridine as catalyst (b).[157]

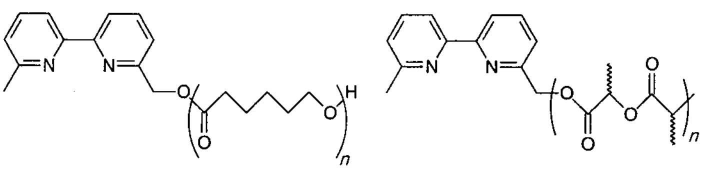


Figure 41. Introduction of metal-binding units into biodegradable polymers.[161]

two bipyridine units connected by a short and flexible spacer belong to this area of research. In their monomeric form, these systems are already well-known in supramolecular chemistry.[1, 4] Eisenbach et al. prepared telechelic polymers consisting of bipyridine and bis(bipyridine) end groups.[162–172] As shown in Figure 42, both types of polymers can be elongated on addition of Cu^I or Ag^I ions by formation of the corresponding metal complexes. The bis(bipyridine)-functionalized polymers form helical structures similar to their monomeric analogues. The resulting coordination polymers were characterized in detail with respect to their mechanical properties and morphological behavior. They were shown to be microphase-separated systems in the bulk, with nano- to mesoscopic superstructures consisting of aggregates of bipyridinecopper complexes in a polyether matrix.

Hosseini and co-workers described a single-stranded helical coordination polymer (Figure 43), as a racemic mixture of left- and right-handed helices, which was obtained by self-assembly of an *exo*-ditopic ligand and silver ions.[173] The structure of the infinite network was established by single-crystal X-ray structural analysis. Although the structure of the coordination polymer was investigated, no information concerning the degree of polymerization was given. In this field of supramolecular chemistry, Stoddart and co-workers described a poly(bis[2]catenane) containing a combination of covalent, mechanical, and coordinative bonds, in which the coordina-

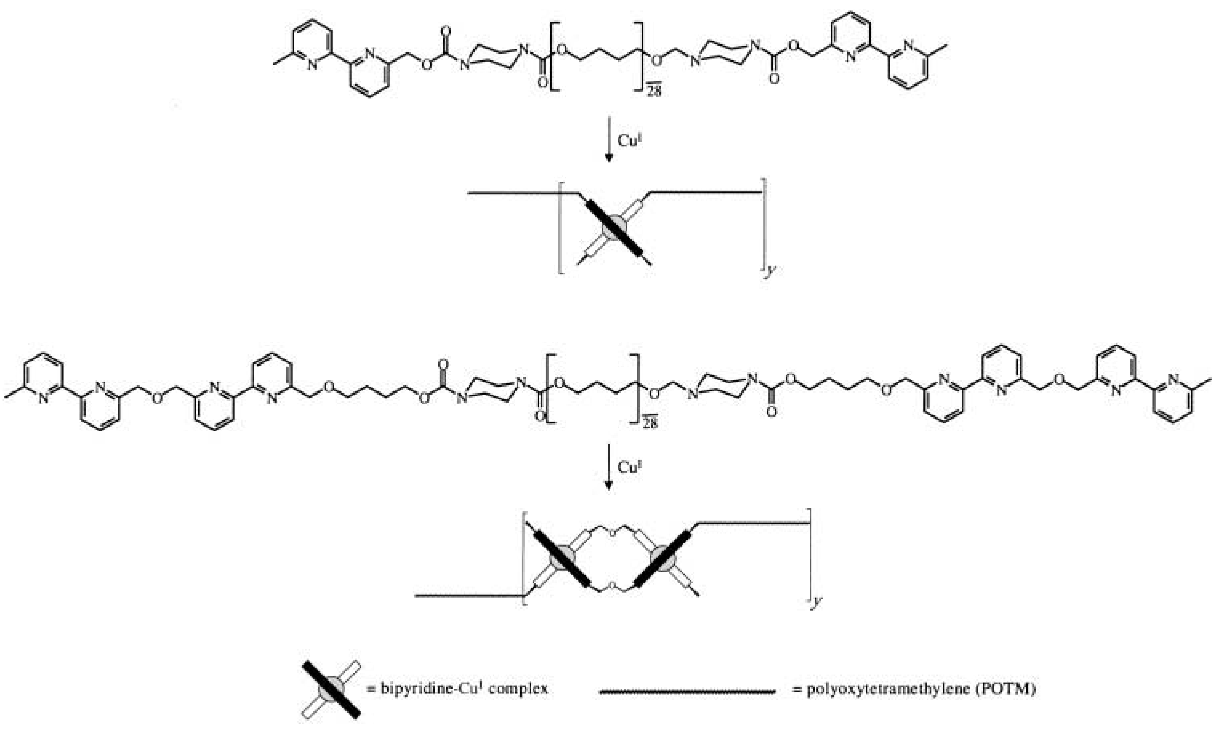


Figure 42. Synthesis of supramolecular (ABA)$_n$ systems by the addition of Cu^{I} ions.[162–172]

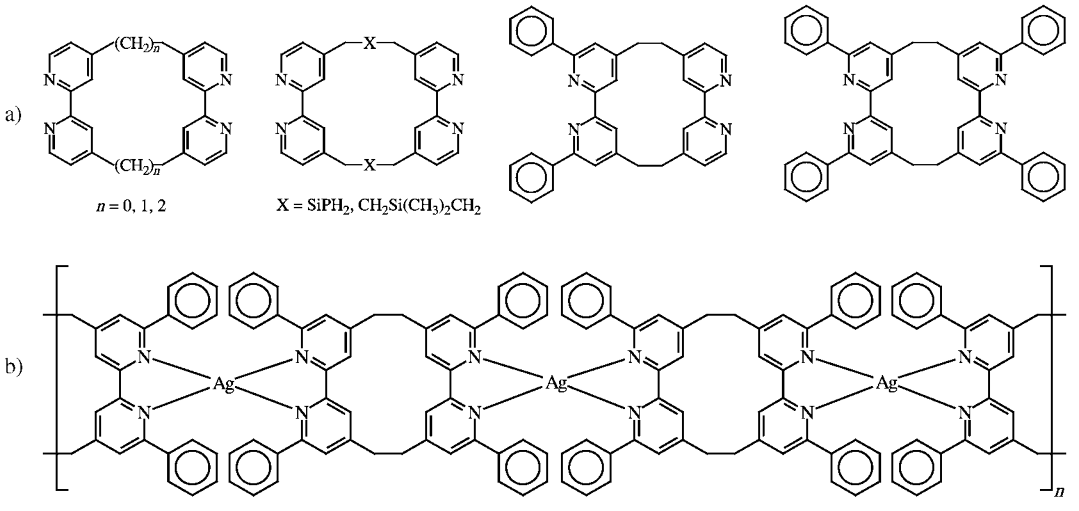


Figure 43. Helical coordination polymer (b) formed by the self-assembly of a bipyridine-based ligand (a).[173]

tive bonds are based on bipyridine – silver interactions.[174] The degree of polymerization was determined to be 40, which is equivalent to a molecular weight of $M_n = 150000\,\text{g mol}^{-1}$.

2.4. Bipyridine-Containing Resins and Beads

Pioneering efforts by Merrifield in polypeptide synthesis made the anchoring of reagents to insoluble supports, known as solid-phase synthesis, popular.[175] In the late 1970s, Card and Neckers were the first to publish a report on bipyridines bound to polymeric supports.[176] Bipyridines were attached after ring bromination and lithiation of polystyrene-divinylbenzene copolymer beads (Figure 44). Shaking a mixture of the polymer and a metal salt in solution led to complexation of the metal ions, and the complexed resin could be easily removed by filtration. The amount of metal ions bound to the polymer was partially controlled by the solvent system because of the different accessibility of the chelating compound. In later works, the same research group prepared zero-valent polymeric metal complexes by chelating, for example, $[Cr(CO)_4]$, $[Mo(CO)_4]$, and $[W(CO)_4]$.[177–179] The catalytic activities for the hydrogenation of alkenes and alkynes based on these systems showed, for example, a turnover number greater than 2800 for the hydrogenation of 3-methyl-3-buten-2-ol.

In 1981, Drago et al. utilized Necker's polystyrene beads to investigate the activity of polymer-bound bipyridineplatinum

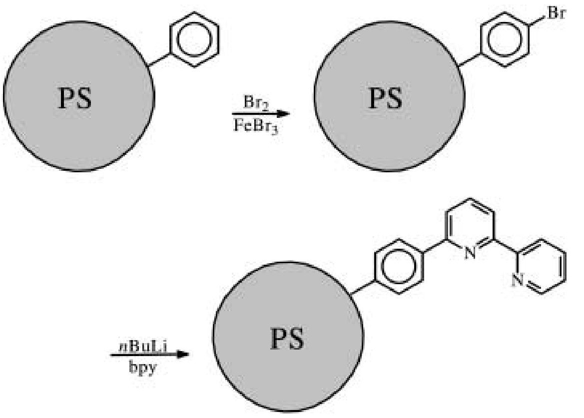


Figure 44. Polystyrene beads containing bipyridine end groups synthesized by Card and Neckers.[176, 179]

and bipyridinerhodium complexes in the catalytic hydrogenation of olefins.[180] Turnover numbers as large as 300 were obtained with the rhodium systems. One year later, Tsuchida and co-workers tried to overcome the reduced activity of the ligands located at the inside of the resins.[181] As shown in Figure 45, they grafted polystyrene beads with soluble oligo(ethylene oxide) spacers to allow the same degree of solvation of the pyridine ligand as in a homogeneous solution. In this case, the beads were cross-linked with 20 mol% divinylbenzene and the complexation behavior with Cu^{II} ions was studied. An apparent formation constant of 11×10^4 s^{-1} was determined for the complex in water, and a stability constant of 4700 $L mol^{-1}$.

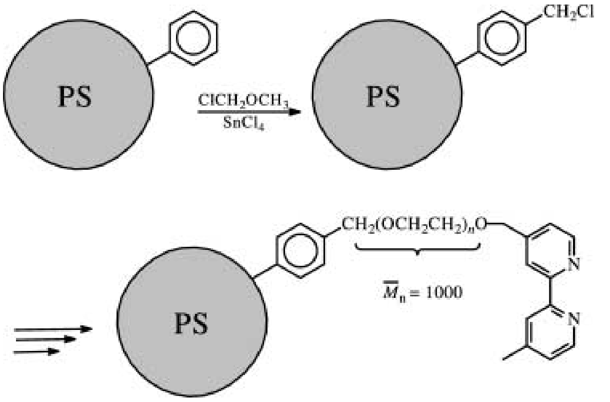


Figure 45. Grafted poly(ethylene oxide) spacers enhance the solubility of the complexing unit.[181]

In their research towards the photochemical behavior of polymers with covalently bound tris(bipyridine)ruthenium complexes, Bourdelande and de March prepared a system with complexes directly anchored to a hydrophobic polystyrene bead.[182] This system was far less efficient than the monomeric $[Ru(bpy)_3]^{2+}$ complex with respect to photoinduced electron-transfer from the complex to methyl viologen. The authors assumed that the hydrophobicity of the polymeric backbone prevented the approach of water-solvated methyl viologen; therefore they introduced, similar to Tsuchida and co-workers (Figure 45),[181] water-soluble tri(ethylene oxide) spacers.[183] However, though they demonstrated the spectroscopic properties of the polymeric Ru^{II}-complexes to be similar to those of $[Ru(bpy)_3]$, the photochemical behavior was different. Therefore, the authors concluded that the applied polymeric supports prevent the bound complexes from being useful for photoinduced electron-transfer reactions. Nakamura and co-workers prepared polymer-bound nitridomolybdenum(VI) complexes by utilizing polystyrene with pendant bipyridine units, similar to the system published by Card and Neckers (Figure 44).[184] The polymeric metal complexes were characterized by photoacoustic and resonance Raman spectroscopy. The hydrolysis and hydrolytic reactions of the complexes, which resulted in the formation of ammonia, were investigated.

By utilizing a more sophisticated system based on colloidal titanium oxide particles, Yoshinaga et al. investigated recently the photochemical behavior of tris(bipyridine)ruthenium complexes bound covalently to these particles.[185] The poly(maleic anhydrides-*co*-styrene)trimethylsiloxane-coated titanium particles were grafted with amino-functionalized copolymers from *N*,*N*-dimethylacrylamide- and acrylate-modified bipyridine (Figure 46). It was suggested that in the course of the photoreaction the excited electron of the complex is transferred to methyl viologen via the titanium surface. The maximum yield of methyl viologen was 6%, but depended on the flexibility of the bipyridine group on the grafted polymer. The quantum yield of fluorescence was less than 0.001.

Thermally stimulated self-aggregation of silica particles was reported by the same research group in 1997.[186] The authors targeted the thermal triggering of particle aggregation by making use of temperature-dependent changes of intramolecular coordination versus intermolecular coordination of certain polymeric bipyridine–metal complexes described by Chujo in 1993.[79, 80] For this purpose, ultrafine colloidal silica particles were coated with trimethoxysilyl-terminated poly(acrylamide-(2-(4-(4′-methylbipyridyl))ethyl acrylate) or poly(*N*-isopropylacrylamide-(2-(4-(4′-methylbipyridyl))ethyl acrylate) (Figure 47). A monodisperse solution of the latter system was stable for 24 h at 15 °C, as indicated by a constant absorption at 500 nm. The absorption decreased when the temperature was elevated to 35 °C. Dynamic light scattering analysis demonstrated that particles in the size range of 1.2 to 1.4 μm were formed.

3. Macromolecules Bearing Terpyridine Units

3.1. Dendrimers with Terpyridine Units

Dendritic structures represent a very special case of terpyridine-containing macromolecules. The following examples are divided into two sections: Dendrimers containing a terpyridine–metal complex inserted at the dendrimer core and dendrimers with terpyridine–metal complexes incorporated in the branching unit or attached to the surface of the molecules.

The use of metal complexes as the core of the molecule provides a convenient opportunity for a convergent synthesis of dendrimers. However, up to now only a few research

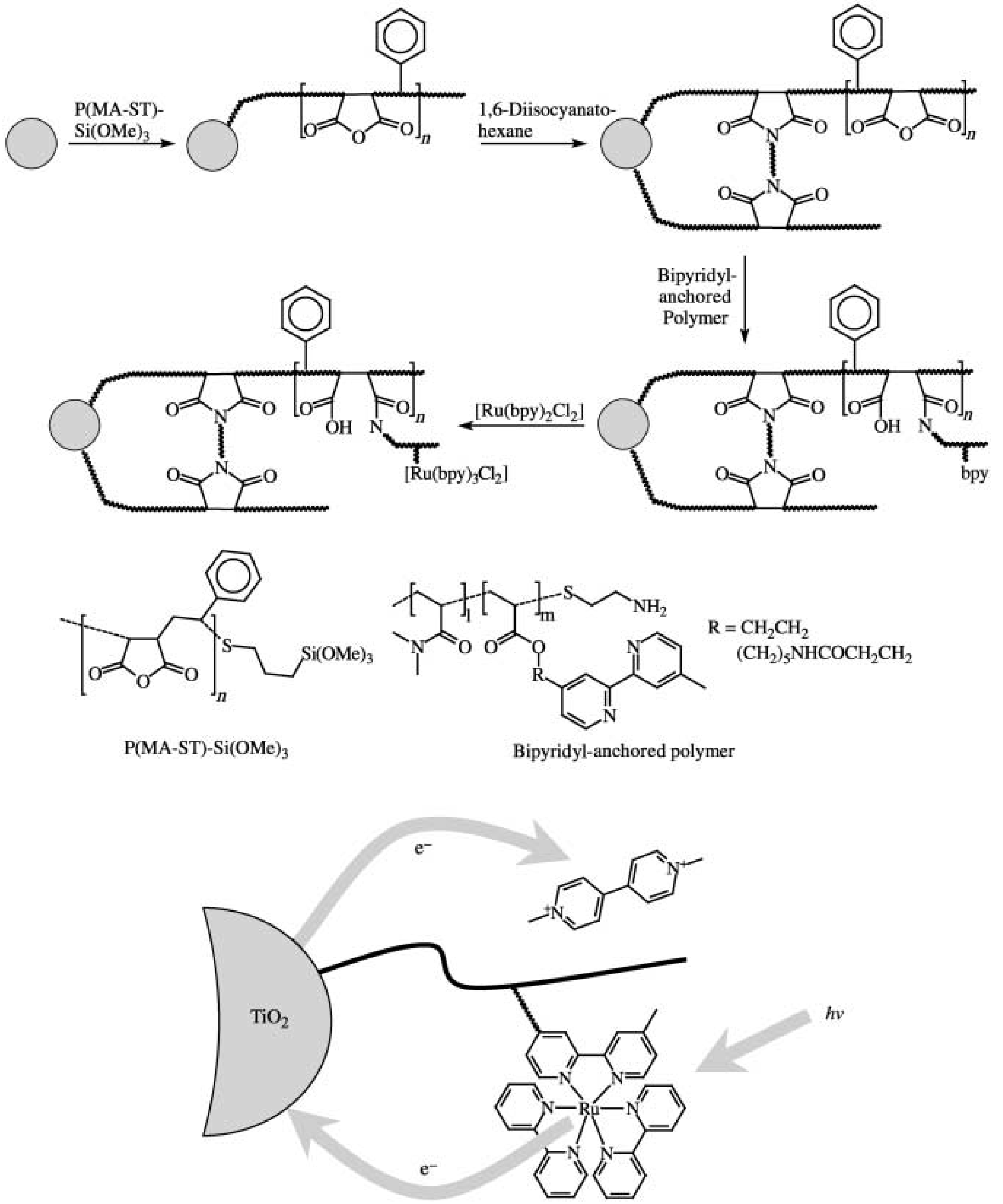


Figure 46. Top: Titanium particles modified with the polymer-grafting $[Ru(bpy)_3]^{2+}$ complex; bottom: suggested mechanism of the photoreaction.[185]

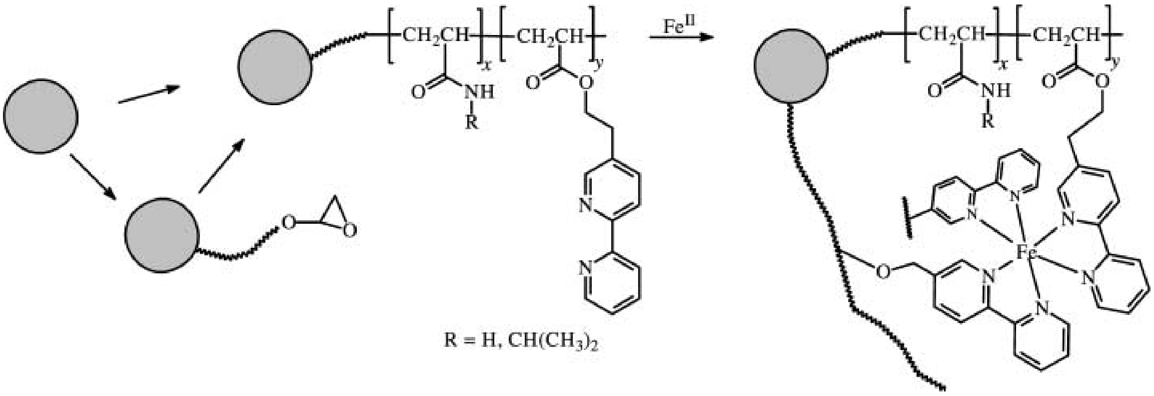
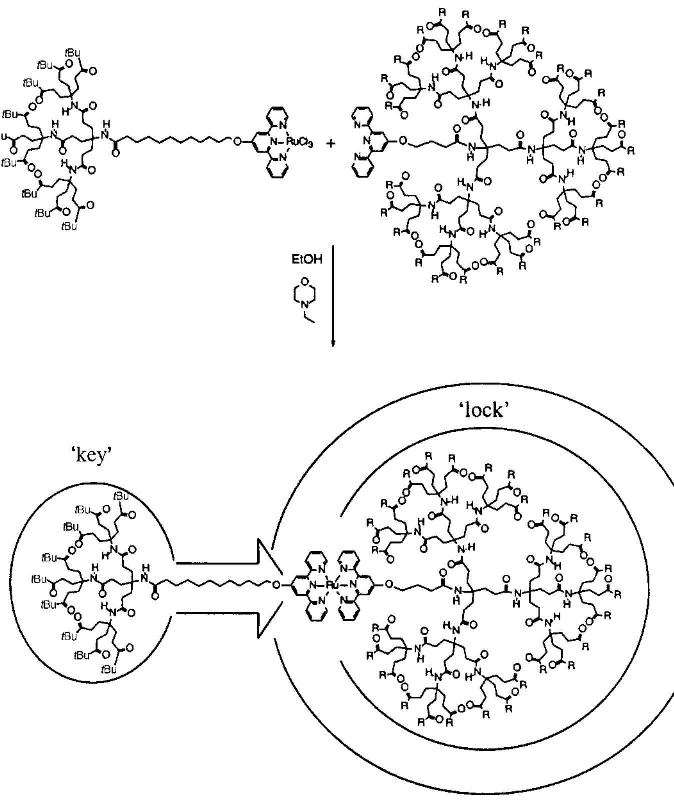


Figure 47. Self-aggregation by ligand exchange among the silica particles in response to temperature elevation.[186]

groups have made use of this strategy. Chow et al. (Figure 48) reported the synthesis and characterization of metallodendrimers with a bis(terpyridine)iron(II) core up to the fourth generation by using benzyl ether based dendritic building blocks with propylene spacer moieties.[187–190] Newkome et al. utilized this principle to connect two independently prepared dendrons in a process that mimicked a key and lock system (Figure 49).[191, 192] Kimura et al. recently connected two 1,3,5-phenylene-based dendrons[193] to form a dendrimer that exhibited one oxidation ($E_{1/2} = +1.12$ V versus SCE) and two reduction processes ($E_{1/2} = -1.28$ and -1.43 V versus SCE). A large voltage difference between the current maximum of the reduction and the oxidation wave (ΔE) indicate a slower electron transfer than in the nondendritic complex.

A special case is represented by the work of Constable et al. in which they utilized a convergent approach consisting of connecting three bipyridine-functionalized arms through the formation of the bipyridine–metal complex to build starlike molecules with a tris(bipyridine)iron(II) or tris(bipyridine)-Co(II) core and bis(terpyridine)ruthenium(II) complexes in the outer sphere.[27, 28, 194] NMR spectroscopy and MALDI-TOF mass spectrometry were used to characterize the resulting species. In the case of the iron(II)-containing dendrimers, the most intensive peak in the MALDI-TOF spectra was exhibited at $m/z = 6330$ Da, which indicates the loss of three PF_6 counterions. For molecules containing the cobalt(II) core, the loss of two to four counterions could be detected.



R = *tert*-butyl, $NHC[CH_2CH_2CO_2C(CH_3)_3]_3$

Figure 49. Lock and key system presented by Newkome et al.[191, 192]

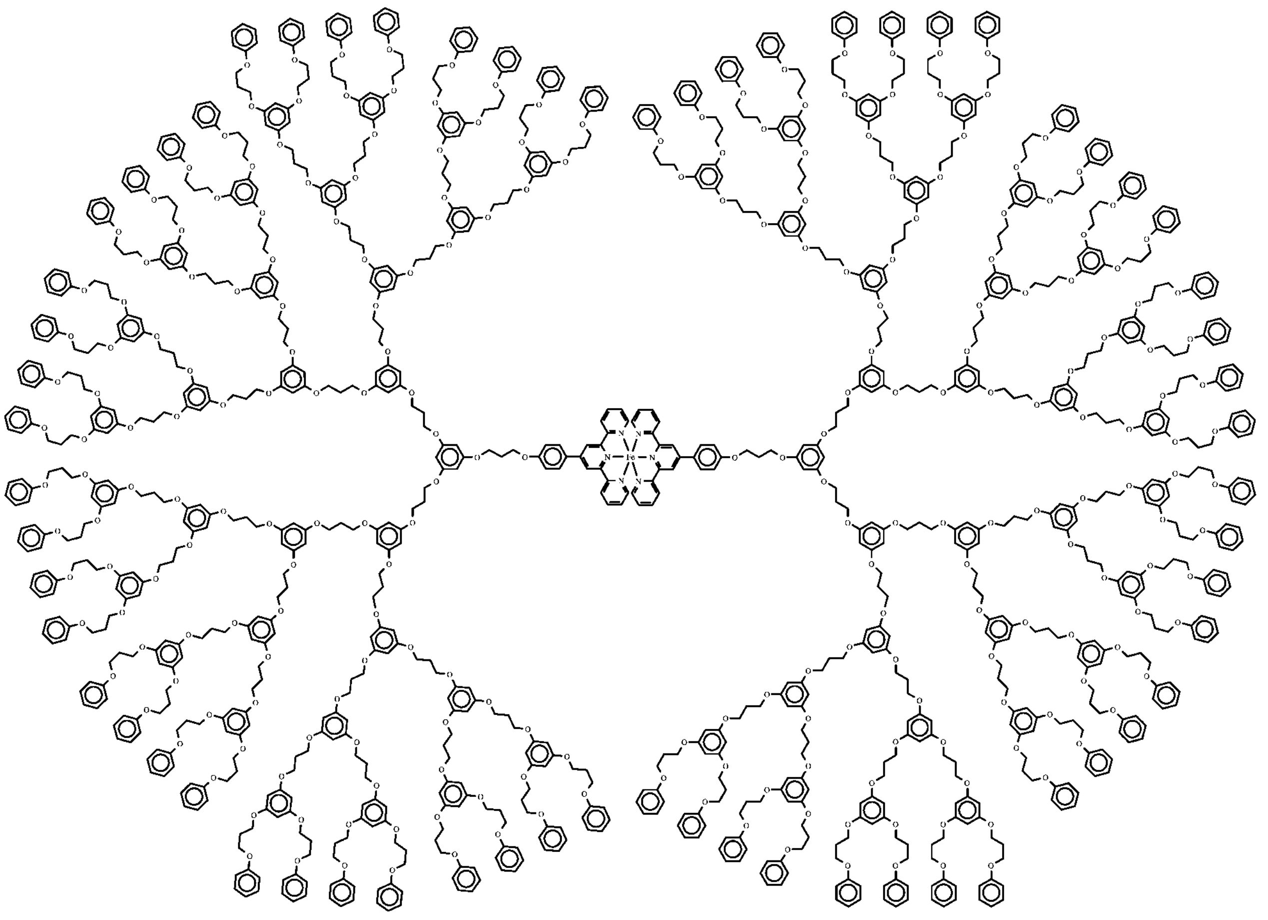


Figure 48. Benzyl ether based dendrimer with an Fe^{II} core.[187–190]

Research on the second category, that is, starlike macromolecules with terpyridine metal complexes in the outer sphere, is being conducted by more research groups.[21, 29–31, 194–202] Some of the published structures have already been reviewed,[20] and therefore we will consider the most interesting and recent publications only. In 1996, Constable and Harverson presented a starlike macromolecule with 18 Ru^{II} centers and 36 positive charges.[198] This molecule, prepared from hexakis(bromomethyl)benzene, possesses six arms, each containing three Ru centers (Figure 50). Constable and co-workers also published a "first generation" starlike system based on pentaerythritol bearing pendant [terpyridine-(4′-[2-(*tert*-butyldimethylsilyl)-1,2-carbaboranyl]-terpyridine]ruthenium(II) complexes.[197] MALDI-TOF mass spectrometry was very useful for characterizating this high-molecular-weight, eightfold-charged system. In a more recent paper, the pentaerythritol core was used for assembling a second-generation hexadecanuclear metallosupramolecular system.[199]

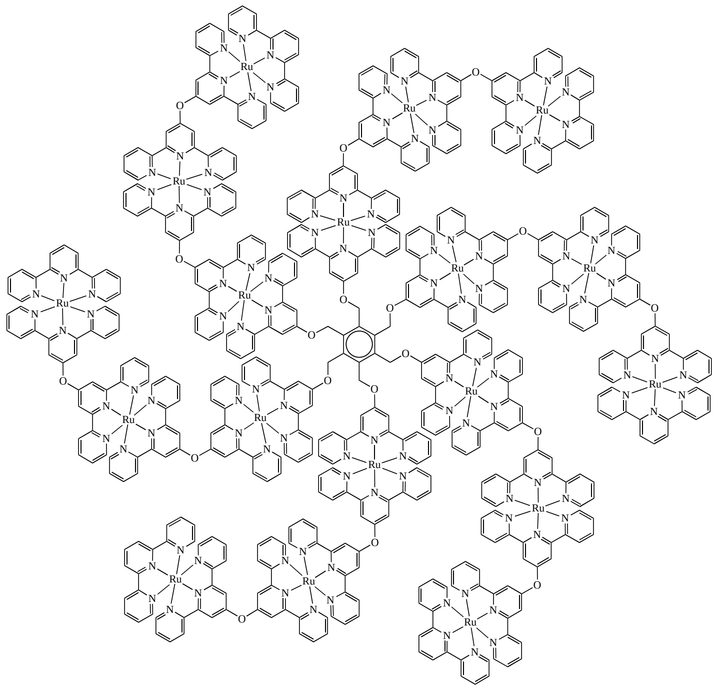


Figure 50. 18 Ru^{II} centers result in a 36-fold positively charged dendrimer.[197, 198]

Tailor-made isomeric metallodendrimers have been synthesized by Newkome et al.[201] The two dendrimers shown in Figure 51 have an identical molecular formula ($C_{597}H_{880}F_{48}N_{52}O_{136}P_{8}Ru_{4}$) and a molecular mass of 12526 Da. The nanoscopic tetrahedral geometry of the methane molecule was mimicked by controlling the design of the macromolecular architecture. While IR, UV, NMR, and MALDI-TOF experiments of the two isomers revealed very similar results, electrochemical studies indicated that internal densities and void regions differ greatly. The voltammograms of both compounds are similar and exhibit two quasireversible waves at negative potentials that correspond to redox processes on the two terpyridine units. The $E_{1/2}$ values of the two waves of **1** ($E_{1/2} = -1.951$ ($\Delta E_p = 0.097$); -1.751 V ($\Delta E_p = 0.109$)) are slightly more negative than these of **2** ($E_{1/2} = -1.923$ ($\Delta E_p = 0.121$); -1.720 V ($\Delta E_p = 0.087$)). The additional difficulty in reducing the terpyridines of **1** could be a result of an increased inaccessibility of the counterions because of the increased dendritic character on the periphery of the molecule. In addition, the ΔE_p values for the two waves of **1** and for the most positive wave of **2** are similar to each other and smaller than the ΔE_p value for the most negative wave of **2**. This result indicates that the rate of electron transfer for one of the terpyridines in **1** is slower than that of the others.

Whereas all other published metallodendrimers utilized counterions such as Cl^-, BF_4^-, or PF_6^-, Newkome et al. introduced a neutral metallodendrimer possessing four bisterpyridineruthenium(II) linking sites.[202] Eight internal carboxylate groups balance the

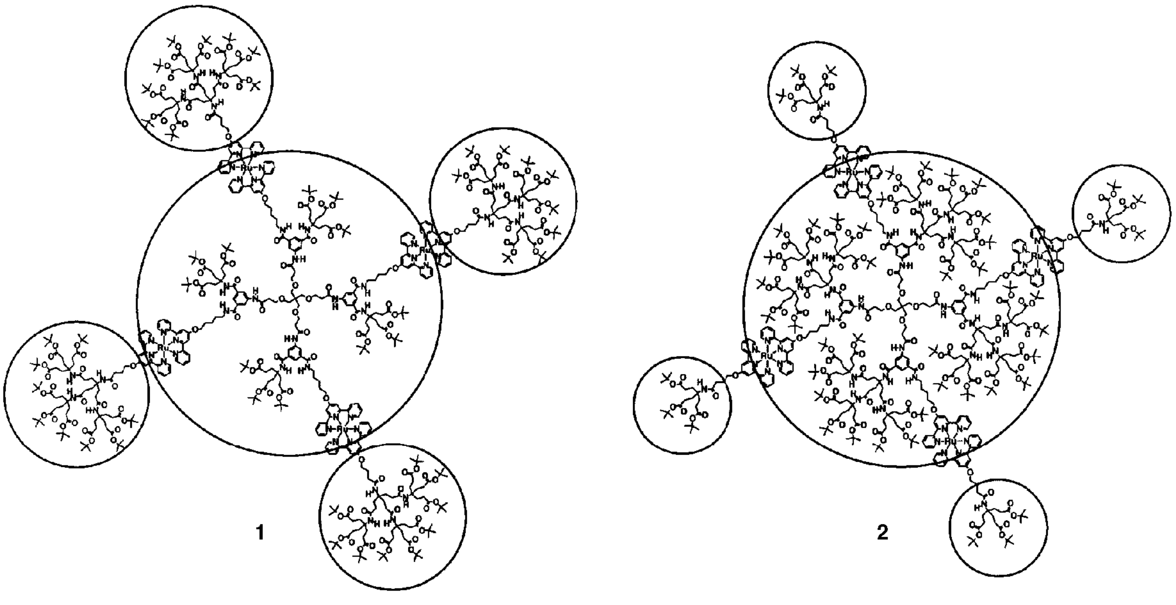


Figure 51. Isomeric metallodendrimers designed by Newkome et al.[201]

charge of the Ru^{II} centers. After dialysis, the characterization was conducted by MALDI-TOF mass spectrometry, UV/Vis, CV, and NMR spectroscopy. Only one signal for the carbon atom was detected for the internal carboxylate group in the NMR spectrum. Poly(amidoamine) dendrimers with an ethylenediamine core were presented up to the third generation by Kimura et al.[195] and up to the fourth generation by Abruña and co-workers.[29–31] The fourth-generation dendrimer contains 64 bis(terpyridinyl)-ruthenium(II) complexes and therefore a total of 128 positive charges. Both groups used peptide-coupling procedures for the synthesis. Abruña and co-workers demonstrated that the interfacial reaction of the terpyridine-pendant dendrimers and a bridging ligand (1,4-bis[4,4″-bis(1,1-dimethylethyl)-terpyridine-4′-yl]benzene) dissolved in CH_2Cl_2 with an aqueous solution of metal ions gave rise to ordered films on highly oriented pyrolytic graphite. STM investigations of these films (Figure 52) demonstrated highly ordered hexagonal 2D domains (in this case dend-8-tpy/Fe^{2+}).[31]

As part of their approach to the preparation of macromolecules with encapsulated silsesquioxanes, Murfee and Hong recently presented dendrimers up to the third generation based on an octa(diphenylphosphanyl)-functionalized silsesquioxane core.[203–205] The third generation was built up by eight dendrons, each possessing four terpyridine molecules to which bis(bipyridine)ruthenium complexes were attached (Figure 53). The molecule thus had 64 positive charges within its outer sphere, which were balanced by PF_6^- counterions. The quantum yields of the dendrimers depended on the generation, but ranged from 0.021 – 0.011. The excited state lifetimes of the ruthenium(II) centers were again dependent on the generation, being 605, 890, and 880 ns (the emission wavelength was 610 nm).

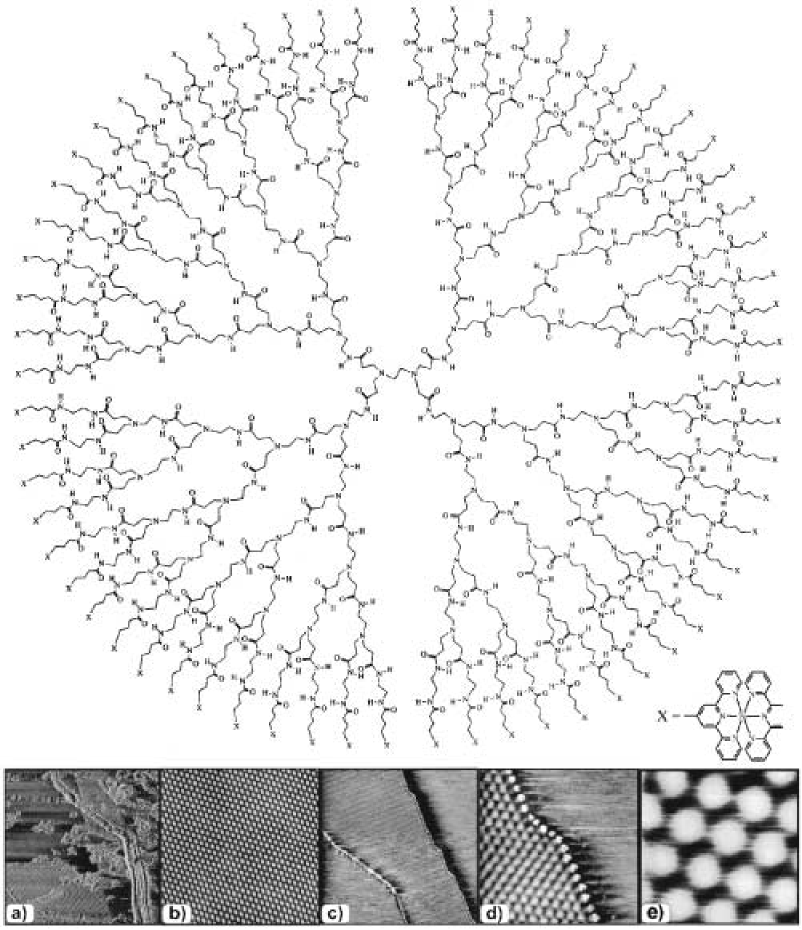


Figure 52. Top: Fourth generation of a dendrimer with pendant bipyridine or terpyridine complexes (X); Bottom: unfiltered STM images of dend-8-tpy/Fe^{2+}: a) 550 nm, b) 200 nm, c) 304 nm, d) 69 nm, e) 26 nm.[29–31]

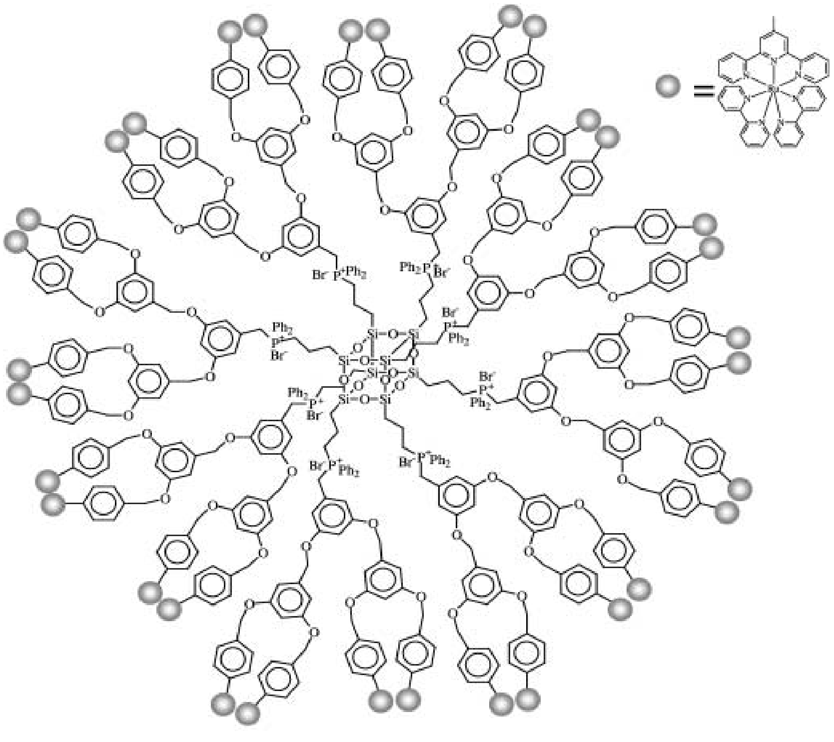


Figure 53. Third generation dendrimer based on a silsesquioxane core.[203–205]

3.2. Polymers with Terpyridine Units in the Side Chain

Potts and Usifer were, to the best of our knowledge, the first to incorporate terpyridine molecules into polymer chains.[206] They homopolymerized 4-vinyl- and 4′-vinylterpyridine by free-radical polymerization, and copolymerized 4′-vinyl-terpyridine with styrene (Figure 54). The resulting polymers were all white powders with molecular masses up to 60 000 $g\,mol^{-1}$ (GPC (polystyrene standard)) and polydispersities in a range of 2 to 44. The addition of metal ions to these polymers resulted in insoluble polymer – metal complexes. The free polymers

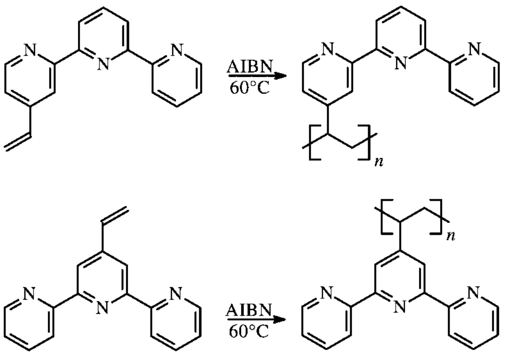


Figure 54. The first terpyridine-containing polymers prepared by radical polymerization of vinylterpyridines.[206]

could be recovered by hot, concentrated hydrochloric acid. Attempts to homopolymerize the corresponding vinylterpyridine–metal complexes failed. In contrast, styrene copolymers were readily formed from (4′-vinylterpyridine)(terpyridine)cobalt(II) hexafluorophosphate and bis(4′-vinylterpyridine)ruthenium(II) hexafluorophosphate complexes.[207]

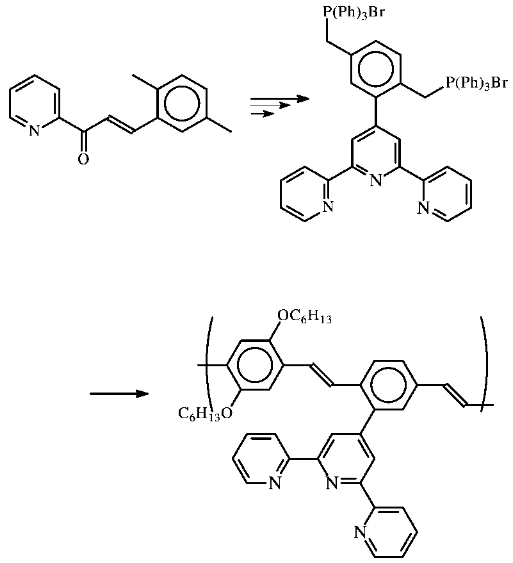


Figure 56. Preparation of conjugated polymers by using the Wittig reaction for an application as fluorescing chemosensors.[210]

A similar but more extended work has been published by Hanabusa et al.[208, 209] in which they prepared 4′-[4-(2-acryloyloxyethoxy)phenyl]terpyridine and copolymerized it with styrene or methylmethacrylate (Figure 55). The average molecular weight, as determined by GPC, was 6400 g mol^{-1} for the styrene copolymer and 15000 g mol^{-1} for the methylmethacrylate copolymer. Later work reported on homopolymers of 4′-(4-styrene)terpyridine, and copolymers with styrene, vinyl acetate, and acrylic acid. While the homopolymers were insoluble, all three copolymers were soluble as a result of their low terpyridine content (5%). In all cases, the corresponding metal complexes were formed with $CoCl_2$, $FeCl_2$, $NiCl_2$, and $CuCl_2$. In 1998, Kimura and Hanabusa et al. introduced a fluorescing poly(*p*-phenylenevinylene) with pendant terpyridyl groups as a chemosensor for metal ions.[210] As shown in Figure 56, polymerization was carried out by a Wittig-type reaction of 2,5-bis(hexyloxy)benzene-1,4-dialdehyde and the terpyridylphosphonium salt to yield a polymer with a mass of 4000 g mol^{-1}, as determined by GPC (polystyrene standard). The fluorescence of the polymer was investigated as a function of various metal ions. The fluorescence at 524 nm was completely quenched by Fe^{II}, Fe^{III}, Ni^{II}, Cu^{II}, Cr^{II}, Mn^{II}, and Co^{II} ions, while a blue shift in the emission spectrum was caused by Pd^{II}, Sn^{II}, Al^{III}, and Ru^{II} ions. Poly(*p*-phenylenevinylene)s with pendant terpyridine ligands were recently synthesized by Wong and Chan.[65] In contrast to the above-mentioned work by Kimura et al.,[210] Wong and Chan did not utilize the Wittig reaction for polymerization, but copolymerized 1,4-divinylbenzene, 1,4-didodecanoxy-2,5-diiodobenzene, and an iodo-functionalized terpyridineruthenium complex in various ratios by Heck coupling (Figure 57). The polymers obtained exhibited photo- and electroluminescence at room temperature. Photocurrent measurements at 490 nm carried out on samples spin-coated onto ITO demonstrated photoconductivities of the order of $10^{-12}\ \Omega^{-1}cm^{-1}$. LEDs produced from these polymers exhibited a turn-on voltage of 5 V with rectification greater than 10^3 at 15 V and a maximum luminance of 360 cd m^{-2}.

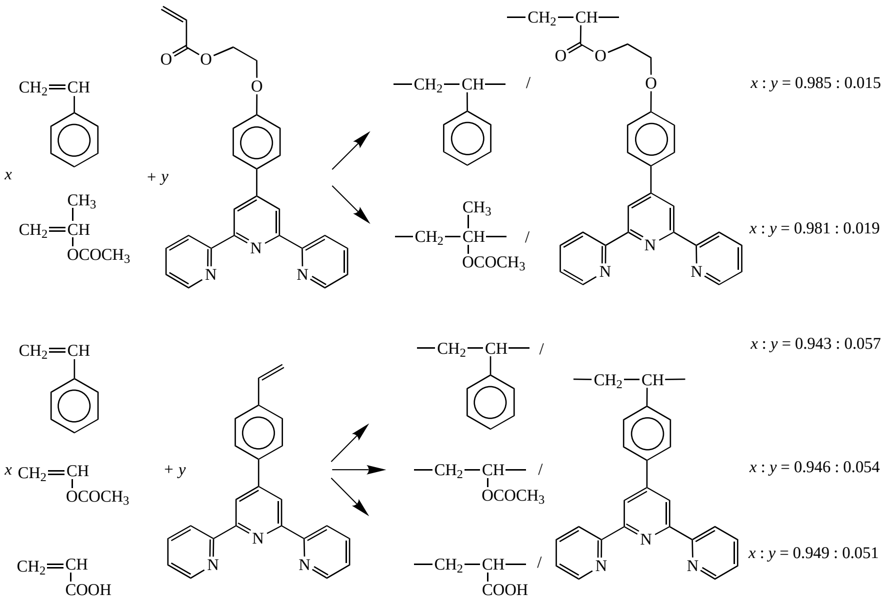


Figure 55. Copolymers with pendant terpyridine units in the side chain.[208, 209]

In a different approach, a dihydroxyterpyridine was treated with a commercially available bisisocyanate-functionalized prepolymer to give an AB multiblock copolymer (Figure 58).[211] The treatment of a solution of the block copolymer with cobalt(II) acetate in chloroform immediately revealed a red-brown color. In contrast to the free polymer, which is a viscous liquid, the complexed material had rubber-like properties.

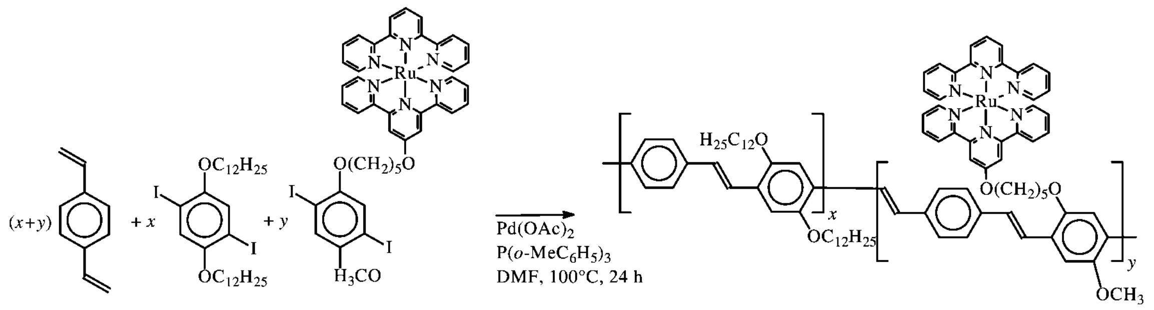


Figure 57. Light-emitting polymers with pendant terpyridineruthenium complexes.[65]

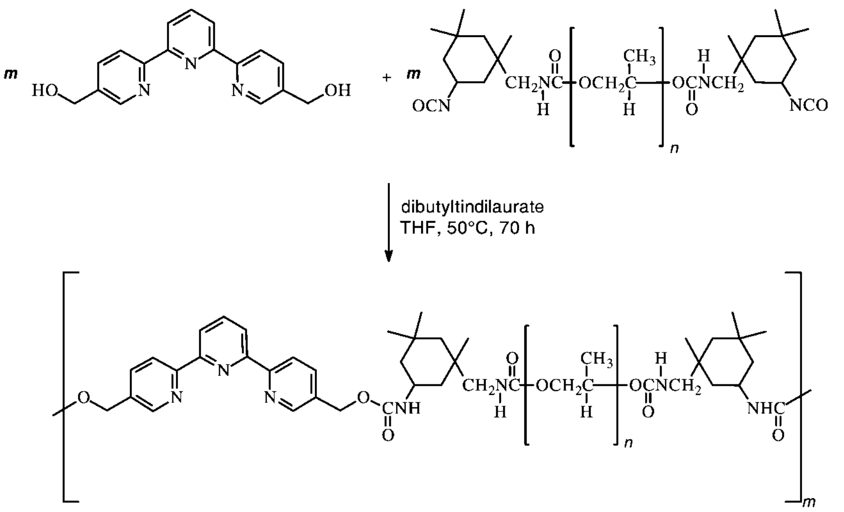


Figure 58. Copolymerization of dihydroxyterpyridine with a bisisocyanate-functionalized prepolymer.

3.3. Polymers with Terpyridine Units in the Polymer Backbone

Polymers with a terpyridine complex in the backbone are rather exceptional. In 1995, Constable discussed, in a small review, his own concept of using metallosupramolecular principles to prepare oligomers and polymers with precoded properties by coordination to metal ions.[212] Although the successful synthesis of a coordination polymer has not yet been reported, the presented structures give a first impression of the potential of this strategy in regard to the incorporation of distinctive physical properties. Some research groups have investigated rigid rods during their research into long-distance interaction phenomena such as electron and energy transfer or magnetic coupling of transition-metal ions.[213] Though no polymers were formed, structures containing functionalized bis(terpyridine) units were obtained which could act as very interesting building blocks for noncovalent polymers.

The research groups of Harrimann and Ziessel are working on building photoactive wires on a molecular scale.[214–221] In 1996, they reported on stiff ditopic ligands and oligomers derived from terpyridines bridged by an alkyne spacer comprised of one to four ethynyl groups.[214] These polyalkynylene chains (Figure 59) allow very fast exchange of electrons between photoactive terminals and prolong the triplet lifetimes by a factor of 3000, relative to the unsubstituted terpyridineruthenium complex. In certain cases, the alkyne bridge undergoes reductive electropolymerization to generate molecular films which contain metal centers dispersed along a conjugated backbone. A major drawback of these rigid bridged systems is that their solubility decreases significantly as the number of acetylene groups increases. To overcome this disadvantage, Khatyr and Ziessel investigated the properties of bis(terpyridine) ligands bearing ethynylenephenylene spacers with solubilizing groups in the 2,5-positions (Figure 60).[218] The lowest energy absorption in these compounds is shifted towards lower energy as the number of repeat units increases. The same correlation was demonstrated for the emission ($n = 1$: 434 nm, $n = 5$: 472 nm). This behavior demonstrates that the electronic communication along the molecular axis is improved as the number of repeat units increases.

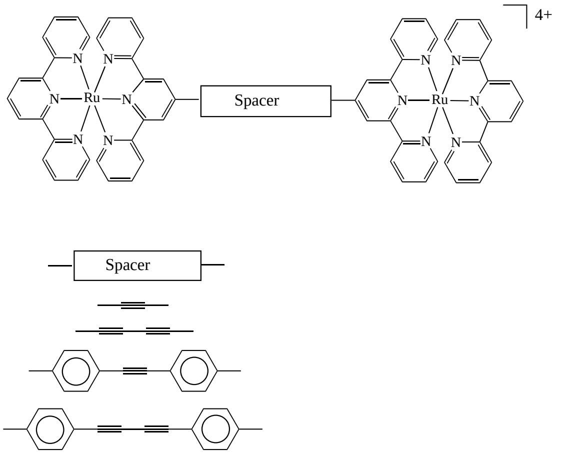


Figure 59. Stiff molecular wires prepared by Ziessel and co-workers.[214–221]

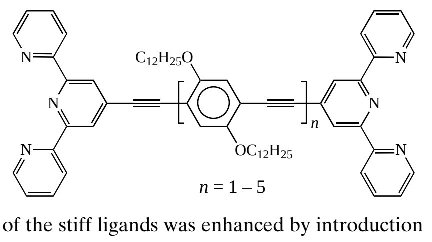


Figure 60. The solubility of the stiff ligands was enhanced by introduction of an alkyl spacer.[218]

The research groups of Sauvage, Barigelletti, and Balzani also investigated rigid ditopic ligands for the construction of one-dimensional molecular arrays.[222–226] To investigate the luminescence and electron-transfer properties, they prepared a ligand consisting of two 4′-(*p*-phenylene)-terpyridine end groups and a bicyclo[2.2.2]octane unit.[224] By this method, strict control over the metal-to-metal distance (2.4 nm) could be obtained and complexes with different metal ions in one molecule could be created. The lifetime of the Ru-based moiety ($\tau = 1.1$ ns) in solution is too short to allow energy or electron transfer. The lifetime is longer ($\tau = 10.5$ µs) in a rigid matrix at 77 K and energy transfer from the Ru-based moiety to the Os-based moiety takes places with a rate constant of 4.4×10^6 s^{-1} (Figure 61). In an earlier publication, a porphyrin was incorporated instead of the bicyclo[2.2.2]octane unit.[223] By utilizing the different complex binding properties, molecules with different metal ions were again prepared. This approach allows the photophysical properties of porphyrin- and terpyridine–metal complexes to be combined.

Bis(terpyridyl)–transition-metal oligomers with up to three metal centers have been reported by Storrier and Colbran.[227] Coupling the aniline group in the heteroleptic bis(4′-(4-anilinoterpyridyl)ruthenium(II) complex with 4′-(4-chlorocarboxyphenyl)terpyridine yielded an amido-linked ligand with a coordinated and a noncoordinated terpyridine domain (Figure 62). Dimers are easily accessible with this ligand by using Co^{II}, Fe^{II}, and Ru^{II} ions to connect the ligands. The application of NMR spectroscopy is of particular interest in examining these complexes, particularly the Co^{II} complex. The paramagnetic ion leads to the signals of the terpyridine hydrogen atoms being shifted downfield by approximately 15 to 90 ppm. Such uncomplexed entities provide interesting building blocks for metallosupramolecular polymers.[228, 229] Starting with 4′-(4-anilino)terpyridine, the polymers were prepared by two different synthetic routes: a) by the coupling of two ligands with difunctional organic reagents (such as pyromellitic anhydride, terephthaloyl chloride or adipoyl chloride) and then treating the new binucleating ligands (Figure 63) with metal ions, or b) preforming monomeric complexes of the 4′-(4-anilino)terpyridine and treating them with the same difunctional organic reagents as mentioned above. In approach b, the polymerization was quenched, and from the end groups a molec-

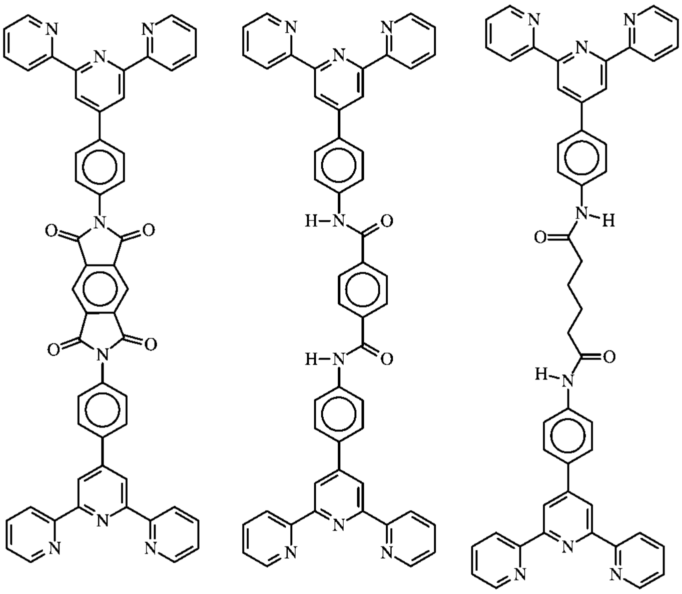


Figure 63. Organic ligands suitable for transition metal ion based noncovalent polymerization.[228, 229]

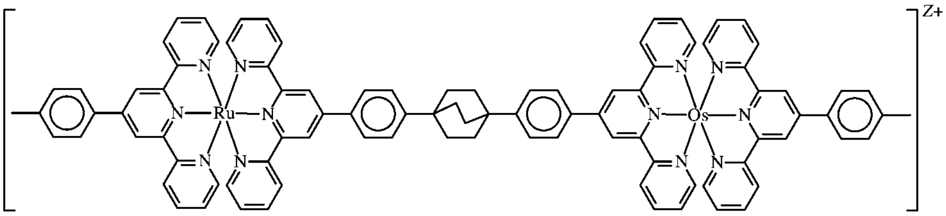


Figure 61. Two different metal ions were held at a distance of 2.4 nm in this photoactive molecule.[222–226]

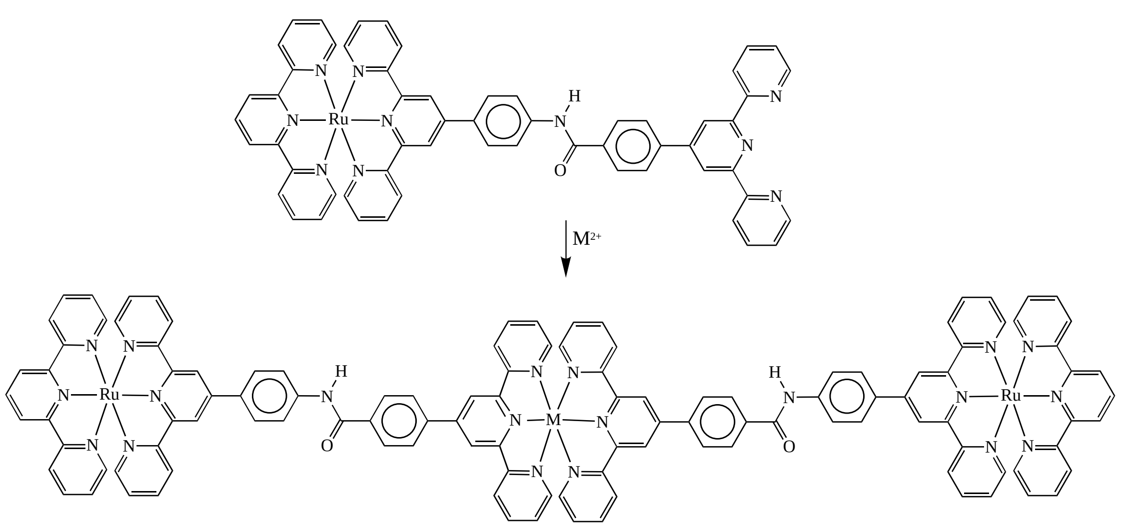


Figure 62. Linear molecules with three metal centers prepared by Colbran and Storrier.[227]

ular weight of 18 kDa, which corresponds to a degree of polymerization of 17, was calculated. Similar results were obtained for the polymers resulting from approach a.

Möhwald, Kurth, and co-workers used analytical ultracentrifugation for the characterization of a coordinating polymer built of 1,4-bis(terpyrid-4′-yl)benzene (Figure 64), first introduced by Constable et al.,[230] and iron(II) ions.[231] By applying the Svedberg formula, they determined a minimum molecular mass of 14900 g mol^{-1}, which corresponds to 25 repeating units. However, this can only be considered as a very rough estimation because of uncertainty in the determination of the compound's partial specific volume.[232] Interesting layer-by-layer self-assembly experiments with this polymer were conducted by Kurth and Osterhout. The resulting alternating monolayers were investigated by X-ray reflectivity measurements, X-ray photoelectron spectroscopy, and surface plasmon resonance spectroscopy.[233] A thickness of dried polymer films of 18 ± 3 Å was determined, which corresponds to a single layer (for the results obtained by utilizing monomeric terpyridine–metal complexes, see ref. [234–238]). Anisotropic thin-film materials of this metallosupramolecular polymer were produced by electrostatic binding to the amphiphile dihexadecyl phosphate.[239] The resulting polyelectrolyte–amphiphile complex forms a stable

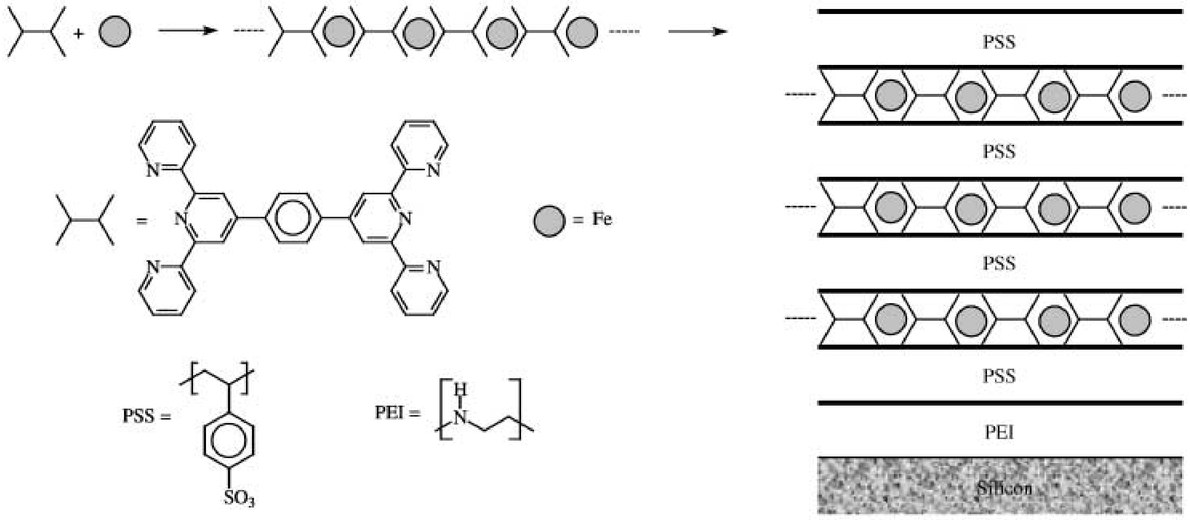


Figure 64. Linear metallosupramolecular coordination polyelectrolytes used for the formation of a superlattice by layer-by-layer self-assembly.[233]

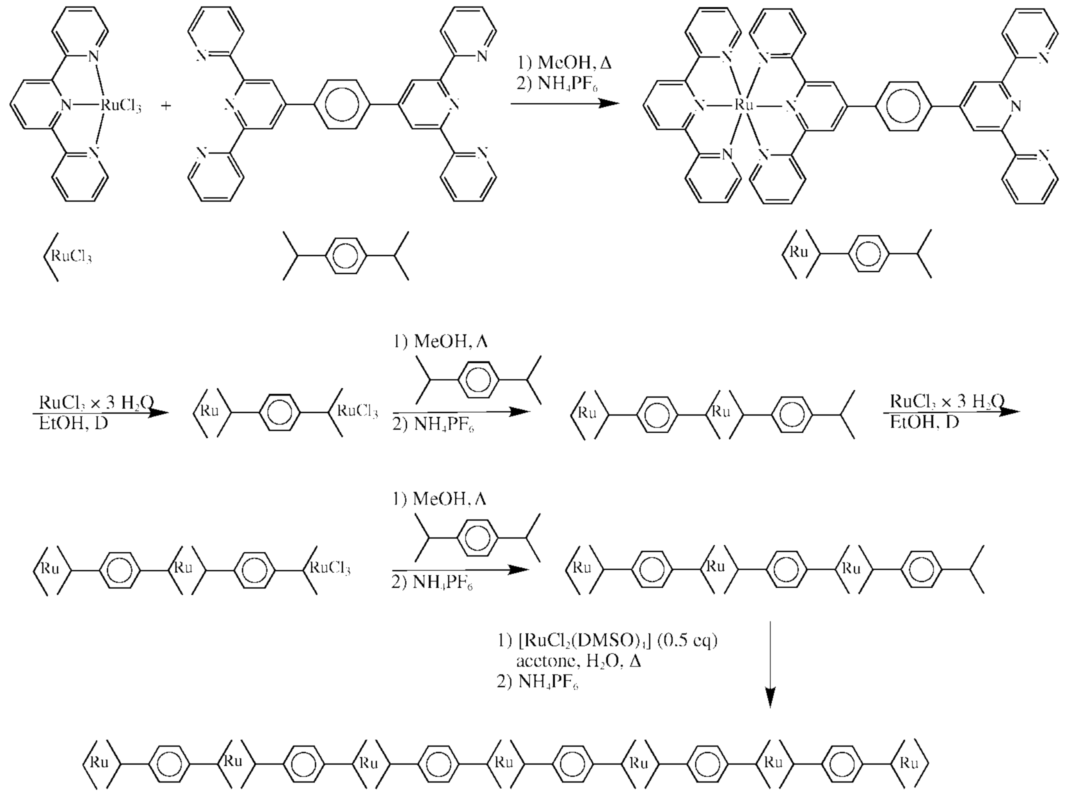


Figure 65. Synthesis of well-defined linear rods consisting of seven metal centers.[240]

monolayer at the air–water interface that is readily transferred and oriented on solid supports by using the Langmuir–Blodgett technique. The average thickness per layer was demonstrated to be 2.8 ± 0.2 nm. The presented strategy opens a new route to materials with tailored structures and functions. The same ligand has been used by Mohler and co-workers for the controlled stepwise self-assembly of rigid rods.[240] A well-defined linear oligomer consisting of seven metal centers was assembled by utilizing ruthenium chemistry (Figure 65). Electrospray mass spectrometry was applied to characterize the heptanuclear complex from a solution in acetonitrile.

A series of poly(*p*-phenylenevinylene) polymers and aromatic polyimides (Figure 66) were synthesized and characterized by Chan and co-workers.[241–244] Poly(*p*-phenylenevinylene)s with the terpyridine complex in the backbone were synthesized by coupling 1,4-divinylbenzene, 1,4-dibromo-2,5-dihexoxybenzene, and bis[(4′-(4-iodophenyl)terpyridine]-ruthenium(II) in different ratios by Heck coupling procedures.[241] The macroscopic properties of the polymers, for example, solubility, changed depending on the monomer ratios. The polyimides were synthesized by the copolymerization of a bis[4′-(4-aminophenyl)terpyridine)]ruthenium(II) hexafluorophosphate complex with different aromatic dianhydride monomers.[242] The electron and hole-carrier mobilities of the polyimides were demonstrated to be of the order of 10^{-4} cm^2 V^{-1} s^{-1}. Single-layered LEDs were produced with an external quantum efficiency of 0.1 % and a maximum luminance of 120 cd m^{-2}. Up to now, the most extensive study on terpyridine-based metal coordination polymers has been performed by Kelch and Rehahn in 1999[245, 246] in which the rigid ligand was functionalized with two *n*-hexyl groups to enhance solubility (Figure 67). From endcapping experiments combined with NMR investigations, the degree of polymerization demonstrated to be at least 30, which corresponds to a molecular weight of more than 36000 g mol^{-1}. These high values were supported by viscosity measurements. The intrinsic viscosity η was determined to be approximately 300 mL g^{-1}, which is in the same order of magnitude as the intrinsic viscosities observed for poly(*p*-phenylene)s.

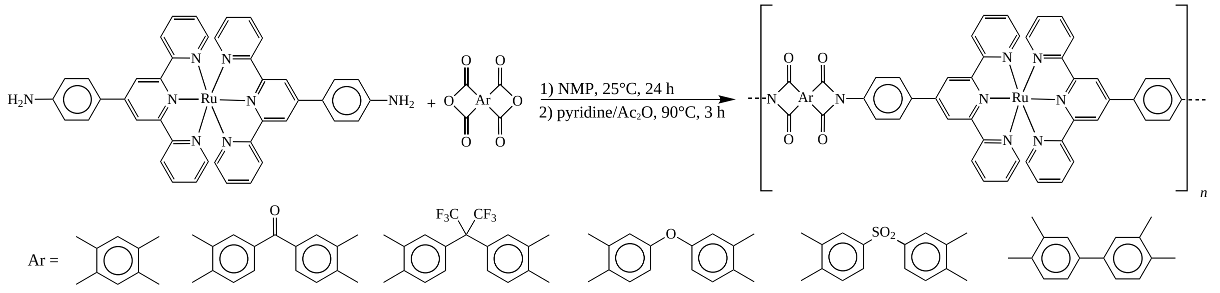


Figure 66. Novel aromatic polyimides for application in LEDs.[241–243]

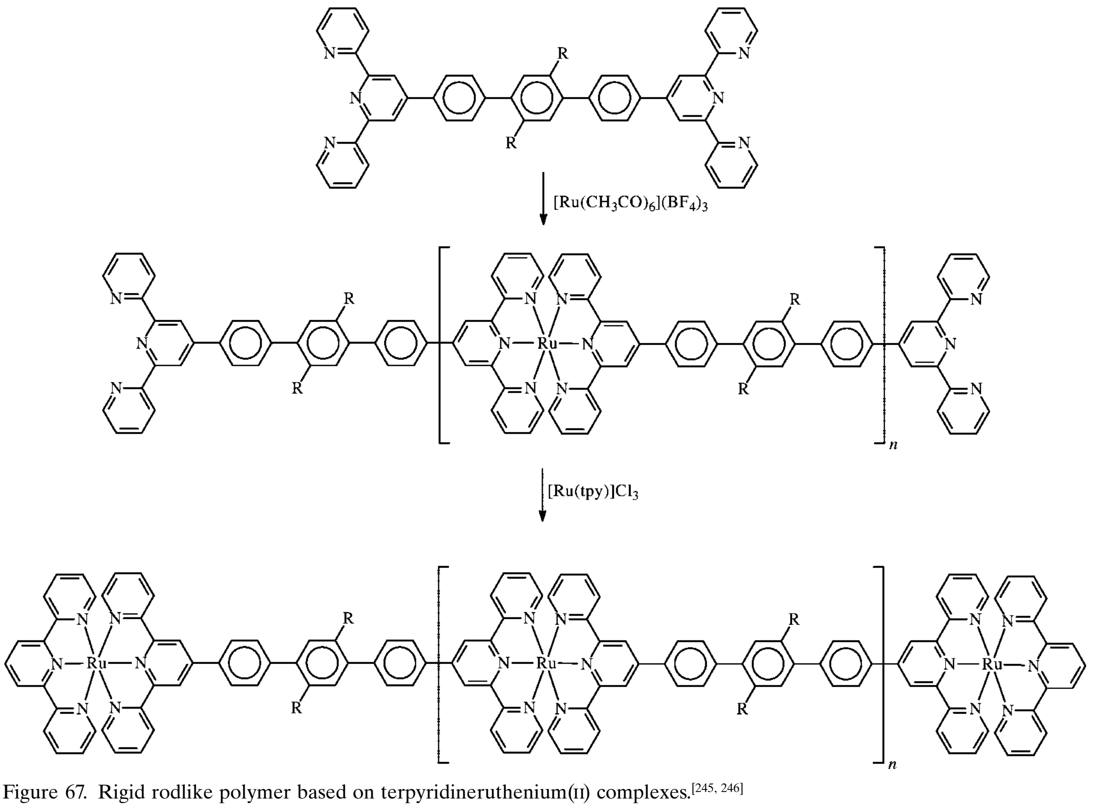


Figure 67. Rigid rodlike polymer based on terpyridineruthenium(II) complexes.[245, 246]

The above described approaches utilizing long side chains to yield soluble rodlike noncovalent polymers in solution have the drawback of using rather complicated building blocks and needing coupling procedures. Recently, a different approach to this class of macromolecules was published: It was demonstrated that 4′-chloro-2,2′:6′,2″-terpyridine can be treated very efficiently with different hydroxy- and thiol-terminated molecules in the presence of KOH in DMSO to yield the corresponding oxo and thioethers in high yields. As a first example a *α*-carboxy-*ω*-hydroxy-functionalized poly(oxytetramethylene) prepolymer was modified in this way with only one terpyridine end unit (Figure 68).[247, 248] The same strategy was then applied to the modification of other different commercially avaliabe bisfunctionalized telechelics, based, for example, on poly(oxytetramethylene) and poly(ethylenoxide) prepolymers (Figure 69).[249–251] In all these cases, MALDI-TOF mass spectrometry proved to be a very powerful tool for the investigation of the resulting modified macromolecules. As shown in Figure 70, the complete bisfunctionalization of the poly(oxytetramethylene) with an average molecular weight of 8000 Da can be easily proven by this technique. The difference in the molecular weights between the prepolymer (top) and the product (bottom) correlates with the complete reaction of two terpyridine units for each prepolymer. In addition, NMR, UV/Vis, and GPC results are also in good agreement with this result. The modification strategy can be easily expanded to other polymeric systems, such as polystyrene, polymethacrylate, or polysiloxanes.

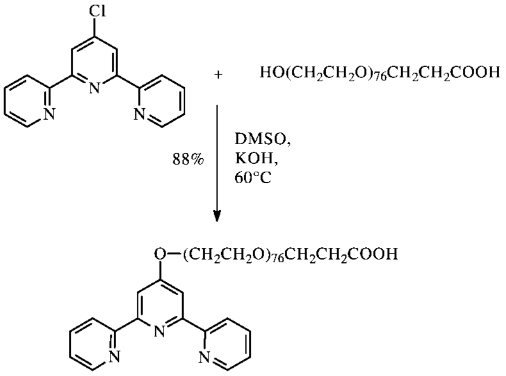


Figure 68. Synthesis of a *α*,*ω*-functionalized polymer.

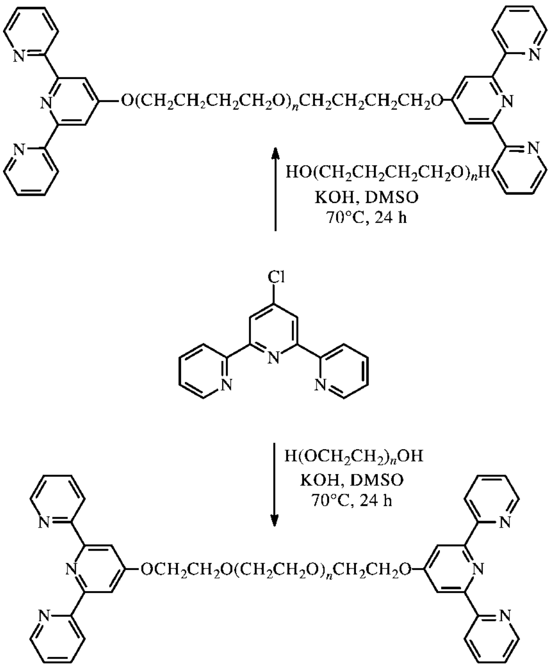


Figure 69. Different metal-complexing compounds.

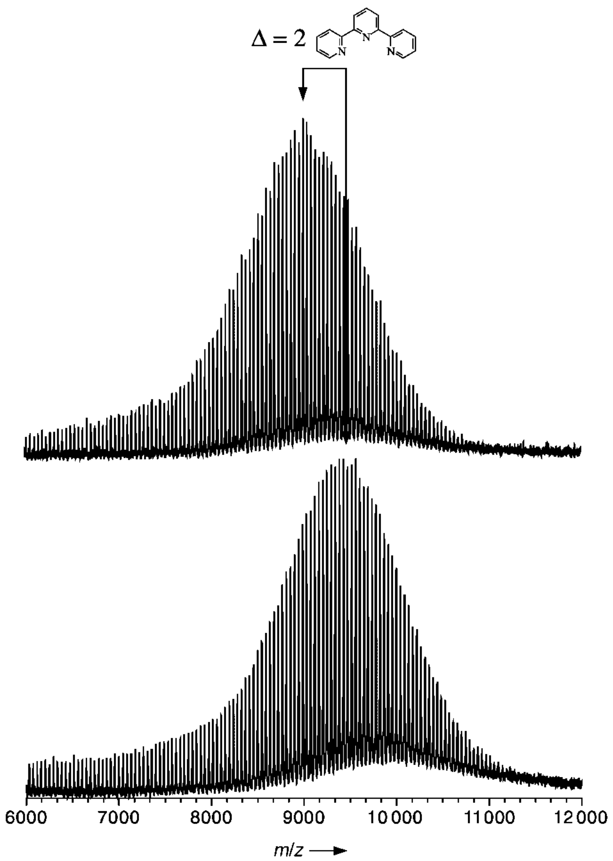


Figure 70. MALDI-TOF mass spectra of the *α*,*ω*-bis(hydroxy)-poly(ethylene oxide)$_{8000}$ (top) and the product *α*,*ω*-bis(terpyrid-4′-yl)-poly(ethylene oxide)$_{8000}$ (bottom; $M_n = 9380\ \mathrm{g\,mol^{-1}}$); the difference in the peak maxima resembles two terpyridine units.

The addition of octahedral coordinating transition-metal ions to terpyridine-modified prepolymers leads to a spontaneous self-assembly of two terpyridine units and therefore to a polymerization (in principle, a polyaddition reaction; Figure 71). The formation of the complexes can be reversed, for example, by changing the pH value[252] or applying electrochemical[253] or thermal changes.[237] The formation of the

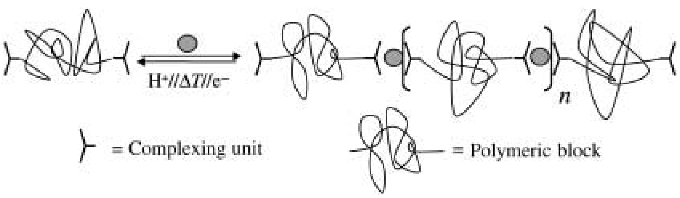


Figure 71. Schematic representation of the noncovalent polymerization.

terpyridine metal complexes and thus the noncovalent coordination polymers can easily be monitored by various techniques, such as UV/Vis and NMR spectroscopy or titration microcalorimetry.

4. Summary and Outlook

The research efforts in the field of bipyridine- and terpyridine-containing ligands and their metal complexes have strongly increased within the last few years. In particular, the central focus has shifted from analytical purposes (complexing of metal ions) to the creation of new materials and supramolecular polymers. However, this development is still at the very beginning, and the first promising results have only been published during the last two years. Certainly there will be a considerable impact of such materials in applications for nanoscience, for tailor-made polymers with tunable properties, and for life-science applications. The first examples can already be seen: such as the temperature and sheer-sensitive starlike polymers from the research group of Fraser, the thermoreversible hydrogels of Chujo et al., the oscillating systems of Yoshida et al., the promising LED devices based on bipyridine–metal complexes by Rubner et al., the stabilization of nanoparticles by coordination of bipyridines on the surface (Chujo et al.), as well as the high-molar-mass metallosupramolecular polymers based on terpyridine metal complexes (research groups of Kurth, Rehahn, Ziessel, and Schubert). A major advantage of these polymer systems over hydrogen-bonded supramolecular polymer systems is the greater stability of the bonds. The use of metal ions has the additional advantage that the chemical and physical properties of the materials can be changed without synthetic expenditure by simply changing the type of metal ions. The future developments in the synthesis and functionalization of suitable metal binding units, the advancements in living and controlled polymerizations, and the progress in modern analytical tools will surely further promote this development.

This study was supported by the Bayerisches Staatsministerium für Wissenschaft, Forschung, und Kunst, the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft (SFB 266, SFB 486, Normalverfahren and Heisenberg Program). We thank Prof. Dr. Dieter Schubert for his help in the preparation of the manuscript and for helpful suggestions.

Received: April 5, 2001 [A465]

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