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Review

Soluble dynamic coordination polymers as a paradigm for materials science

Viviane A. Friese [a], Dirk G. Kurth [a,b,*]

[a] *Max-Planck-Institute for Colloids and Interfaces, Am Mühlenberg 1, 14476 Golm, Germany*
[b] *National Institute for Materials Science, Organic Nanomaterials Center, 1-1 Namiki, Tsukuba 305-0044, Japan*

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Contents

Abstract

Metal ion induced self-assembly of polytopic ligands can be employed to make macromolecular assemblies in solution. This new class of coordination polymers has recently attracted increasing interest. By carefully adjusting the boundary conditions of self-assembly it is possible to form soluble macromolecular assemblies in solution. For this, the binding constants between metal ions and ligands have to be of the appropriate strength. If the interaction is too weak, macromolecular species will not form, but if it is too strong, precipitation may occur. Intermediate binding constants imply a facile exchange of ligands, that is, soluble coordination polymers are generally dynamic equilibrium systems. Through the design of the ligands, the choice of the metal ions and through the pH, ionic strength, temperature and other experimental parameters it is possible to define a window of opportunity where soluble coordination polymers exist. However, the dynamic nature poses a great challenge for characterization because structure and property depend on the external conditions. Besides the value-adding properties of transition metal ions such as electrochemical, magnetic, optical and reactive parameters these polymers add a dynamic component to an already rich spectrum of polymer properties. The dynamic nature makes them unique for fundamental research to address questions concerning self-assembly thermodynamics and kinetics. Additionally, these polymers provide an enormous potential for the development of stimuli-responsive and intelligent materials.

Keywords: Supramolecular chemistry; Coordination polymers; Reversibility; Self-healing polymers; Molecular magnets; Spin transition

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1. Introduction

Polymers play a substantial role in the modern society due to the vast variety of their physical and chemical properties as well as their wide spread commercial application [1]. Traditional polymer science is concerned with covalently formed polymers, where the monomers are linked by covalent bonds [2]. The so formed covalently bonded polymers have well-defined (static) molecular weight distributions that define their physical properties. During the last decades, attention has turned to a new class of polymers, supramolecular polymers in general and coordination polymers in particular. Here, self-assembly has been adopted for the synthesis of different polymers (Fig. 1). There are different non-covalent interactions available for these types of polymer assemblies. The most utilized example is hydrogen bonding [3], but also π–π-stacking [4], van der Waals interactions [4] and metal ion coordination have been used. It is the latter that we will be most concerned with in this review. The fusion of traditional polymer chemistry with supramolecular chemistry results in a generation of materials that are designed to use direc-

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[*] Corresponding author. Tel.: +49 331 567 9211; fax: +49 331 567 9202.
E-mail address: kurth@mpikg.mpg.de (D.G. Kurth).

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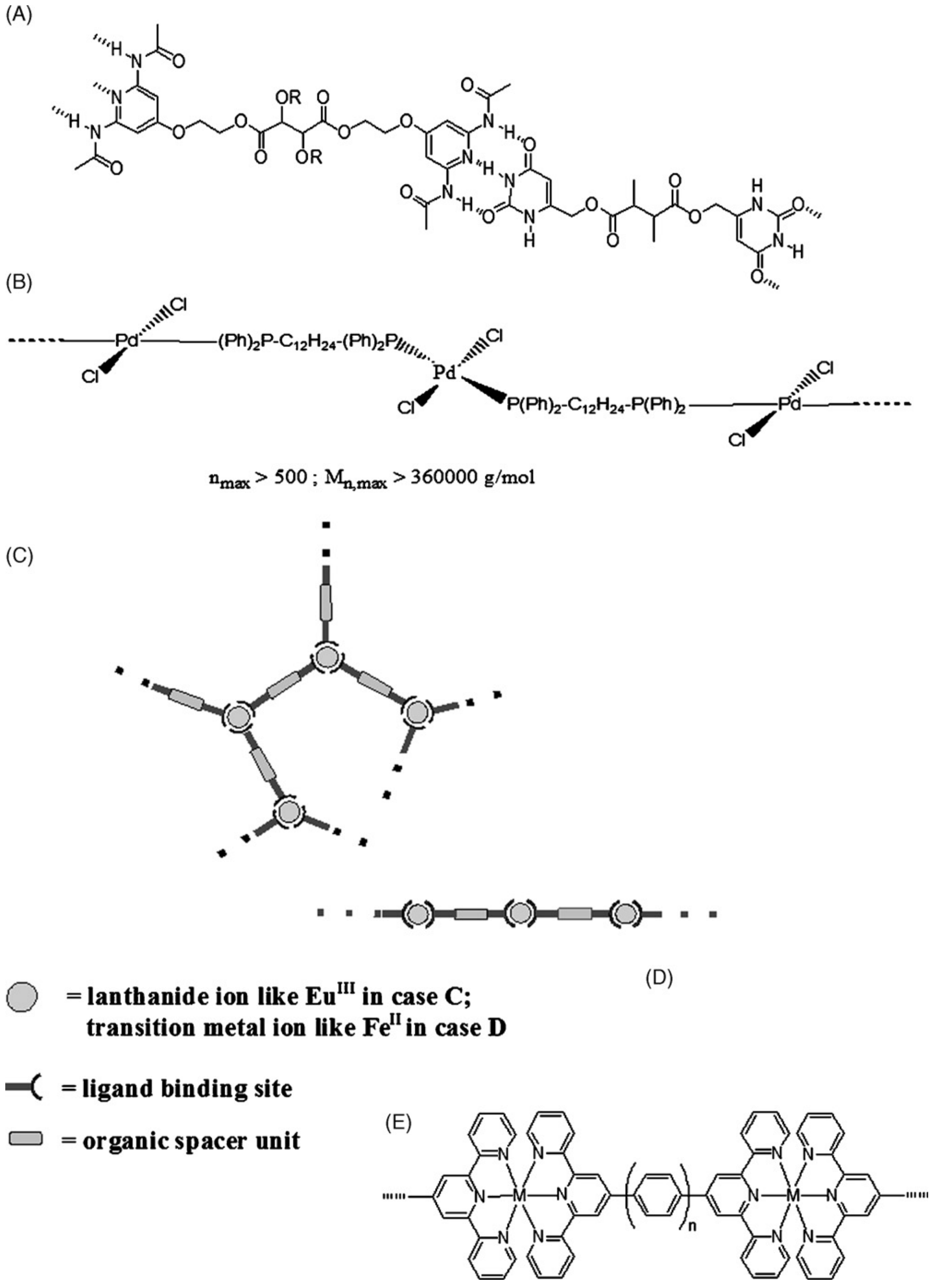

Fig. 1. (A) Example of a supramolecular polymeric system, showing complementary synthons and their multiple hydrogen bonding (adapted from Ref. [4]). (B) Metal-ion induced bonding in a coordination polymer, adapted from Ref. [7]. (C and D) Schematic representation of reversible polymer architectures obtained from different metal-ions with ditopic ligands. (E) Example for a linear coordination polymer like (D).

tional interactions and recognition processes on the molecular level [5]. Lehn recognized early on that it was helpful to consider these materials as (virtual) dynamic combinatorial libraries [6]. Most important in this approach is the reversibility of the interactions, that leads to dynamic systems whose properties depend on the extent of the reversibility. It also is a means to control/manipulate features such as chain length and geometry, thus allowing for subsequent rearrangement at the molecular level.

Dynamic coordination polymers (DCPs) can be considered a fusion of traditional organic polymers with inorganic coordination chemistry. These polymers are now intensely studied due to their unusual properties provided by the metal ion, e.g. molecular-magnetism [8–13], synthetic metallic conduction [14–17], non-linear optics [18–21] and ferroelectrics [22–25], and this, in combination with the outstanding mechanical properties of conventional polymers. The possibility to modify their magnetic, electric and optical properties as well as their morphology by the choice of the involved metal ions and the manipulation of its redox properties in addition to the ligands opens pathways to a completely new class of functional materials. Of special interest are here supramolecular coordination polymers that are formed spontaneously in solution via a metal ion induced self-assembly process [26]. Furthermore, we will focus on polymers that assemble from molecular components rather than polymeric ones. For the last example, the reader is refereed to the reviews by Schubert and co-workers [27]. For the systems discussed here, it is the metal-to-ligand binding that acts as driving force for the polymerization of polytopic ligands and metal ions [28]. This class of coordination polymers and the chemistry and physics behind their outstanding properties will be the main focus of this review.

2. Coordination polymers and their self-assembly

Transition metal coordination polymers are systems in which the polymer chain is built-up by the formation of coordinative bonds, e.g. metal ions and ligands form Lewis-like acid–base pairs in which one partner acts as a donor and the other as an acceptor to form a dative bond [29]. In inorganic chemistry, infinite 1D, 2D and 3D coordination networks that are formed in the solid state are considered to be coordination polymers. Typical inorganic metal–organic-frameworks (MOFs) are isolated and analyzed as crystalline solids with properties that are very promising for applications such as gas storage. (For details about MOFs, the reader is referred to one of the excellent reviews on the topic [30–32].) For this review, however, only species that retain their polymeric nature in solution will be considered. We therefore exclude those materials that exist in polymeric form only in the solid state, and form due to lattice energy considerations alone. The building blocks used to make MOFs have generally very small binding constants and do not form polymers in solution but assembly occurs only in the solid state. Also, we will not consider assemblies that consist of only a few repeat units. Due to their dynamic nature as discussed below, the degree of polymerization of coordination polymers depends on the experimental conditions. However, at the appropriate conditions, metal ion induced self-assembly can result in macromolecular assemblies with molecular weight distributions rivaling that of traditional covalent polymers. Only such systems will be considered here. Also an important issue in coordination polymer science is solubility. To be a useful coordination polymer, the compound needs to be soluble in an appropriate solvent. It is a well-known problem that the insolubility of the compounds currently known results in a profound lack of structural information [33]. One reason for that is that a large number of these polymers are built-up by the use of organic bis(polydentate) ligands as connecting units between metal ions. These ligands often contain planar aromatic rings, which have a tendency for π-stacking that results in compounds that are either insoluble or precipitate before they can attain a higher molecular weight [34]. In the case of rigid molecular ligands and highly charged polymers, this issue is a particular concern. There are two classes of soluble transition metal coordination polymers: (a) those that are based on kinetically inert transition metal complexes, which are stable in solution and are thus readily characterized by standard polymer analytical tools and (b) those based on kinetically labile transition metal complexes, that form soluble equilibrium polymers under appropriate conditions. In the former case, we usually deal with second and third row metals like Pt, Pd or Ru that provide substitution inertness [35]. Synthesis of these polymers generally does not occur under ambient self-assembly conditions due to the slow ligand-exchange kinetics. The resulting polymers may, therefore, not be dynamic equilibrium systems. The latter usually contain first row metals in their typical +II or +III oxidation state. In general, these metals exchange their ligands more rapidly so self-assembly occurs under ambient conditions and the polymers can be considered equilibrium or quasi-equilibrium polymers. The kinetics for metal–ligand exchange reactions depend on the metal ion. In the case of high molecular weight polymers, the polymer may not be at equilibrium due to the large numbers of interactions involved. Nevertheless, such a polymer can show all the characteristics of a dynamic material and will respond to external stimuli. The assumption that decomposition (disassembly) occurs exclusively via ligand replacement reactions as stated by Rehahn et al. leads to two possible routes to study DCPs, one of which would be to exclude all coordinating solvents or other molecules that could compete with the ligands for the metal ion [36]. On the other hand, chelating polydentate ligands can be used with binding constants that exceed the ones of other competing molecules, solvent or otherwise.

In case of neutral ligands, the resulting coordination polymer is also a polyelectrolyte, due to the charge of the metal ions. Polyelectrolytes are macromolecules that are soluble in polar solvents like water in which they dissociate into poly-ions having multiple charges and a corresponding amount of smaller ions carrying a lower charge of opposite sign [28]. Between the charged polymers, long-range electrostatic interactions are operative so that structure and property also depend on the ionic strength of the solution. In fact, the charge of the resulting polyelectrolytes may contribute to their stabilization in solution due to repulsion as in colloidal solution [37,38]. Because these compounds are rather soluble in polar solvents, the solvent molecules are also coordinating and compete with the ligands for the metal ions. In order to obtain a dynamic system with a sufficiently high degree of polymerization (DP), the stability constant, K, of the metal–ligand interaction needs to be high enough to hold the polymer backbone together even in solution.

In a first approximation, the degree of polymerization of a single component self-assembling polymer is connected to the stability constant by the relation: $\mathrm{DP} \sim K \cdot [M]^{1/2}$ where $[M]$ is the monomer concentration. This relation implies that, even at moderate concentrations, high molecular weight polymers can only be obtained at large K ($\mathrm{p}K > 10$) values. Now, one might ask why to use such systems as they form only under particular conditions and are moreover difficult to characterize. The answer would be that it is their dynamic behavior that is the basis of the most appealing property of these systems: the reversible assembly–disassembly process. This process, which will be dealt with in more detail later on, means that at equilibrium the bonds in the polymer backbone are subject to a constant breaking and reformation process on an experimental timescale, resulting in, for example, the potential to incorporate additional processes like self-repair or self-healing. Moreover, the equilibrium can be interfered with deliberately through an external stimulus. Finally, it should be noted that it is possible to switch the binding interactions for instance by electrochemically changing the redox state of the metal ion. Thus, there are many ways to tinker with the equilibrium and the therefrom resultant properties! As a consequence, these materials do not have static properties such as a well-defined molecular weight like covalent polymers. In fact, asking for the molecular weight makes sense only if a particular equilibrium condition is fulfilled so that the system is at a particular concentration, stoichiometry, ionic strength, pH and so forth. Finally, besides the thermodynamic properties, the kinetic properties can also be adjusted. This means that the way the system responds to an external stimulus can be controlled in phase and amplitude. For applications, DCPs can be tuned such as to respond in a meaningful and intelligent way to changes in the environment. When the polymer is built-up from kinetically labile metal complexes in the backbone, the obtained system is an equilibrium polymer with a metal–ligand interaction showing the aforementioned breaking and recombining on the experimental time scale. Weak, competing interactions add an important new quality to the already rich properties of polymers. It also means that due to the aforementioned assembly–disassembly equilibrium, a coordination polymer can be switched from the monomeric (disassembled) to a polymeric (assembled) state by a suitable external signal, giving rise to strong non-linear properties, for instance viscosity.

Using arguments from thermodynamics, it is possible to compute the molecular weight of coordination polymers (Fig. 2) [39]. Here, the binding constants of terpyridine and Fe(II) were used as an example [40]. Polymer growth occurs in two steps, the binding of a metal ion to a ligand and the consecutive binding of a second ligand to this unit. Both steps are characterized by a binding constant. A repeat unit is defined as one ligand and one metal ion while the stoichiometry is defined as the ratio of concentrations of metal ion to ligand, respectively.

As expected, the maximum molar weight, shown as average number of repeat units, peaks at a 1:1 stoichiometry. We note that no polymers form if the ligand is in excess ($y < 1$). On the other hand, the system is tolerant to an excess of metal ions ($y > 1$). In the vicinity of $y = 1$, we can expect strong non-linear properties, e.g. if the redox state of the metal ions is changed. Also shown is the molecular weight as a function of the concentration for different values of the stoichiometry, y. The molecular weight depends on the concentration and the stoichiometry. In the case of $y = 1$, we observe exponential growth of the polymers as the concentration increases. It is interesting to note that if the stoichiometry, y, deviates from 1, polymer growth stops if one component is consumed, and the molecular weight remains constant even if the total concentration is increased (plateau region). By adjusting the stoichiometry it is possible to control the molecular weight! So metallo-supramolecular coordination polymers can form very high molar masses if the metal ion, the ligand, and the concentration – as the length depends critically on concentration – are chosen appropriately. For the present case, it is advantageous if the second binding constant is larger than the first, because the second reaction constitutes the growth step. In case of rigid-rod type polymers, we can anticipate additional effects that will affect the assembly process, such as the formation of lyotropic phases.

Unfortunately, the dynamic nature also means that DCPs are not easily characterized, because their equilibrium is dependent on and influenced by concentration, pH, solvent, ionic strength, etc. Every method that disturbs or displaces the equilibrium in either direction, as, for example the interaction with a surface of a column material in chromatography, will lead to results that may not reflect the state of the polymer under consideration. It is, therefore, necessary to use several different complementary methods to obtain meaningful results for the analysis of such dynamic systems. Additional problems during characterization may arise from the polyelectrolyte character of DCPs as their properties become dependent on the ionic strength of the solution thus adding another variable to be investigated. Nevertheless, several methods are now available that allow us to interrogate the state of these polymers in solution or on surfaces. Neutron and X-ray scattering techniques can be used to obtain information about the size and shape of the macromolecules and the hierarchical structures they form. NMR is another technique to investigate DCPs that does not interfere with the equilibrium. However, NMR is generally limited to diamagnetic metal ions although exceptions exist. Analytical ultracentrifugation is yet a technique that can be used to determine the molecular weight of dynamic coordination polymers in solution under various conditions. It was shown to be a reliable technique for these systems as the interference with the equilibrium is minimal so that it can be used for the characterization of molecular properties that cannot be carried out with any other technique [42]. However, it should be pointed out that due to signal-to-noise and signal strength

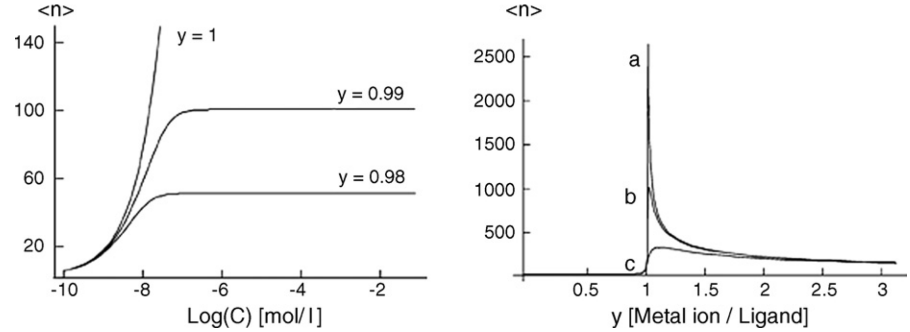

Fig. 2. (Left) Average number of repeat units $\langle n \rangle$ in an assembly (in arbitrary units) as a function of stoichiometry, y, for different monomer concentrations (right: (a) 10^{-3} mol L^{-1}; (b) 10^{-4} mol L^{-1}; (c) 10^{-5} mol L^{-1}) and concentration for different stoichiometries (left) [41].

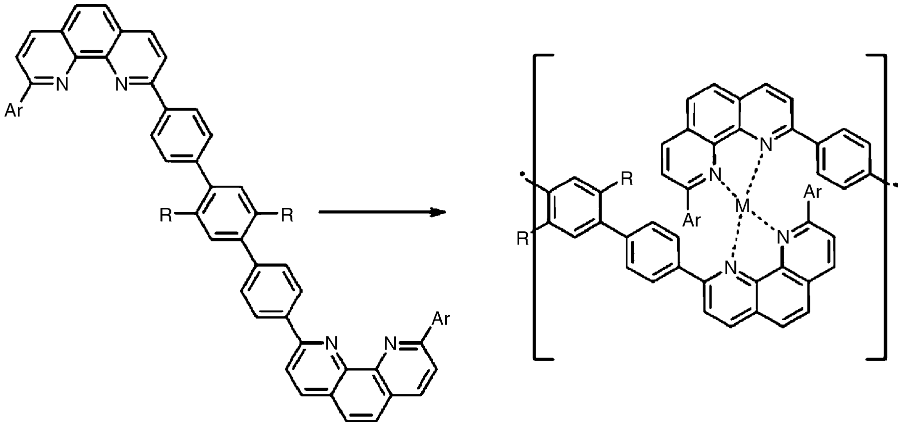

Fig. 3. Kinetically labile coordination polymers based on the ditopic phenanthroline ligand and Cu(I) and Ag(I) ions [36].

considerations each of these methods can only probe a limited window of concentration. The concentration, solvent, ionic strength or other parameters cannot easily be altered without shifting the equilibrium. Viscosity measurements are frequently used for the molecular weight determination of DCPs, but for this method a suitable standard needs to be established first in order to extrapolate the molecular weight from consecutive measurements of the studied system [43]. While TEM has been used extensively for polymer characterization, it has not been used much for DCPs. AFM is a technique that can be used to analyze these polymers on surfaces, e.g. with respect to length, stiffness, and morphology [44]. However, evaporation of the solvent may induce polymerization and therefore the polymers on the surface do not necessarily reflect the length in solution. In contrast to their characterization, preparation of DCPs is straightforward: polymer formation occurs spontaneously through self-assembly of metal ions and ligands in solution under ambient conditions. Publications on dynamic coordination polymers (DCPs) are still rare and only recently have synthetic as well as analytical strategies been developed to study such systems [34,41]. In general, these systems are built-up from polytopic ligands, that can have identical or different metal ion receptors and, depending on the aimed-for coordination number, a range of metal-ions can be used to obtain tetra-, penta- and hexacoordinated complexes. Additionally, functional groups and spacers can be incorporated into the ligands to define structural properties, e.g. flexible or rigid, or to add other functional features (Fig. 3).

3. Examples

To avoid ligand exchange in solution, Rehahn developed a synthetic strategy using only non-coordinating solvents, assuming that the coordination polymer decomposed exclusively via displacement of the ligands by the coordination of solvent molecules. So in a non-coordinating solvent, ligand-exchange should be reduced and hence the polymer forms and can be characterized. However, most polyelectrolytes prefer polar solvents and are poorly soluble in organic solvents. This problem can be avoided by the introduction of alkyl side chains to the ligand to increase its solubility in organic solvents. The authors could indeed show that their coordination polymer forms polymeric species in a non-polar solvent like 1,1,2,2-tetrachloroethane (TCE). On the other hand, they have shown that in the presence of coordinating solvents such as acetonitrile or pyridine, lower molecular weight species are favored. Another, more recent, typical example for such a dynamic coordination polymer is the system introduced by our group [45]. Here, the coordination polymer is built-up from a rigid ditopic ligand that, combined with an appropriate amount of first row transition metal ion, spontaneously assembles into a linear, rigid-rod type, positively charged polymer (Fig. 4). This linear arrangement is due to the octahedral coordination geometry of the metal. However, the ditopic ligand must be rigid enough to prevent ring formation; otherwise lower molecular weight species will be favored due to entropic reasons [46].

The investigated system is water-soluble; such systems are easy to handle and well suited for industrial applications on a large scale because they do not produce large quantities of organic solvent waste. Importantly, the chain length of these polymers varies with the metal to ligand ratio, with the maximum chain length being obtained when roughly equimolar amounts of metal ion and ligand are used.

If instead of a first row transition metal a lanthanide metal ion is used together with a ditopic ligand, then the outcome is a completely different one: because these metal ions can accept nine coordinative bonds, they can bind to three instead of only two ligands, resulting in a 3D polymer network instead of linear chains, depending on concentration (Fig. 5) [47].

At this point, we encounter another variable in these systems: the ligand geometry. With the rigid-rod type ligand used

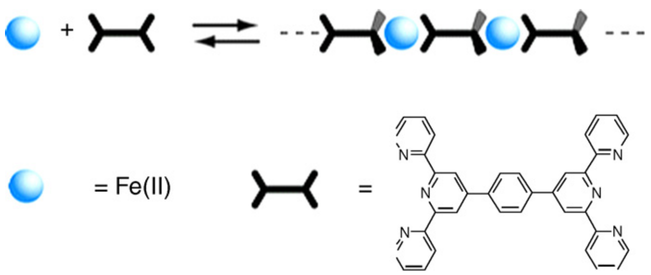

Fig. 4. Metal-ion induced dynamic self-assembly of linear coordination polymers with ditopic ligands and metal ions [41].

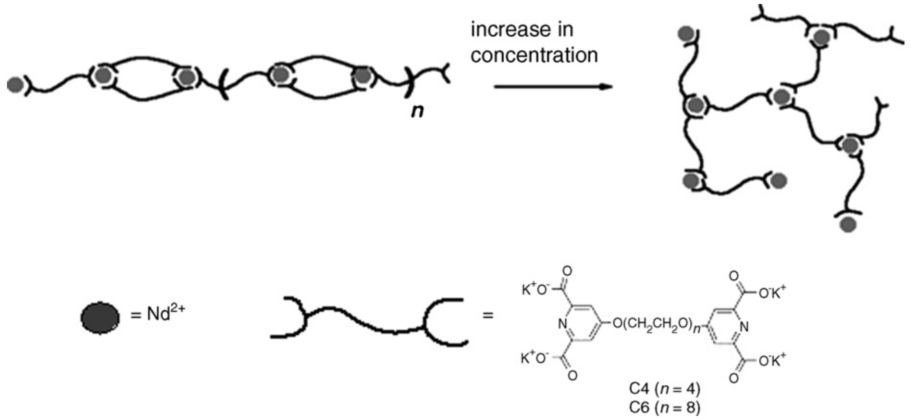

Fig. 5. Structural characteristics of Nd^{3+} coordination aggregates as a function of concentration (adapted from Ref. [47]).

to form the metallo-supramolecular polyelectrolytes (MEPEs) mentioned earlier, high molecular weight rods are formed exclusively. However, in the case where a more flexible spacer connects the two binding sites of the ditopic ligand, much lower molecular weight species are formed when metal-ion and ligands are brought together. This is due to the difference in the ligand geometry. In the first case, the short and stiff spacer connecting the bonding functionalities of the ligand only allows for a linear arrangement, whereas a longer and more flexible spacer results in more degrees of freedom for the arrangement of the system. The latter leads to the formation of rings, which is not possible in the case of the rigid rod like spacer, and the subsequent lowering of the average molecular weight. Vermonden and co-workers have shown, that the length of the spacer, the metal to ligand ratio and the ligand concentration all influence the geometry of the obtained coordination polymer with linear, network and different ring size structures all being possible. These examples already sufficiently demonstrate how carefully a system must be chosen in regard to its desired properties. Many influencing factors must be considered in choosing the right components and much work still needs to be done to fully understand the ways in which it is possible to control and manipulate these systems. However, the fact remains that these systems can be used to obtain materials that are responsive to variations in concentration, temperature, mechanical strain and other external parameters due to the dynamic character of the assembly–disassembly equilibrium. They can, therefore, be adaptive, allowing for the tuning of, for example, electrochemical, photophysical and mechanical properties in response to external changes, in addition to self-healing abilities [48,5].

One of the problems that arises during the synthesis of this kind of system is the contamination of the reaction mixture with monofunctional metal ion receptors, with functionality here defined as the number of bonding groups per monomer unit. These monofunctional contaminants can be a synthetic byproduct from the synthesis of bifunctional monomers and are difficult to get rid off due to the similarity of the chemico-physical properties of the mono- and bifunctional ligands [49]. Because a monofunctional receptor terminates polymer growth, their presence in the reaction mixture causes the average chain length to decrease and therefore lowers the average degree of polymerization, which earns them the name chain-stoppers. On the other hand, chain-stoppers can also be added deliberately as a means of control over the chain length. To be able to do this, the relation between the amount of chain-stoppers added and the resulting chain length must be established. For this purpose, Stuart et al. investigated the effect of the addition of chain stoppers on the average chain length by vapour pressure osmometry and static as well as dynamic light scattering. Theoretical calculations predicted that the number-average degree of polymerization $\langle N \rangle$ should be proportional to $1/x$, with x being the mole fraction of chain stoppers within a certain range of concentration. This corresponds with the experimental results for one of their investigated systems while in the other case investigated, the chain stopper is assumed to form aggregates which decreases its effectiveness as a chain stopper. The authors found that the chain stopper effectiveness can be influenced by several factors: The association constant of the chain stopper with the supramolecular polymer must be infinitely high and at the same time, the chain stopper should only associate with one side of the growing polymer chain. They also state that the effectiveness of a chain stopper is dependent on the properties not only of the chain stopper itself but also of the growing polymer chains. Due to the difficulties of removing chain stoppers that have not been added deliberately, Stuart et al. also developed a new method to selectively remove these chain stoppers by an induced phase separation. Their concept consists of the use of a poor solvent to induce a phase separation to obtain a polymer rich and a polymer poor phase. The latter, containing most of the monofunctional contaminants, can then be discarded. They additionally introduced a theoretical model to numerically calculate phase diagrams for ternary mixtures containing the solvent as well as the mono- and bifunctional ligands. With these calculations, the separation process can be directly derived from the obtained phase diagram (Fig. 6).

More importantly, the authors were able to describe a mathematical model in terms of only three variables: C_0, D_0 and α (C_0 and D_0 being the concentration of the bifunctional monomer in the two coexisting phases and α being the ratio of the slopes of the tieline (DC) and the dilution line (SC) in the above shown phase diagram). On the basis of their calculations, the authors estimated that with this purification method the chain stoppers

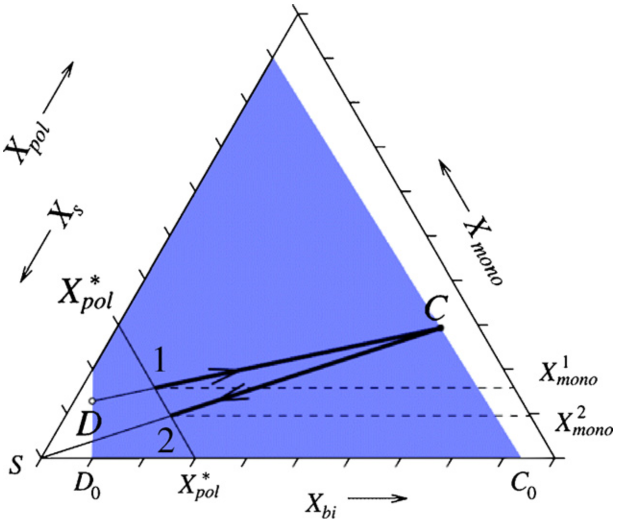

Fig. 6. Schematic representation for the purification method. The tieline shown in this figure is tilted for clarity. The total polymer content $X_{\mathrm{pol}} = X_{\mathrm{bi}} + X_{\mathrm{mono}}$ is equal to $1 - X_{\mathrm{s}}$, so the X_{pol} axis runs in the opposite direction from X_{s}. The purification is started in point 1 at a certain total polymer mole fraction X_{pol} and monofunctional monomer concentration X_{mono}. Point 1 lies within the phase separated region and will therefore spontaneously separate into compositions C and D. The dilute phase is removed, and the concentrated phase is diluted with solvent along the SC line, until the total polymer concentration is again equal to X_{pol} (point 2). Note that $X^2_{\mathrm{mono}} < X^1_{\mathrm{mono}}$ because the dilution line SC is steeper than the tieline DC [49].

can be removed with 99% efficiency in one to two purification steps while still retaining 80% of the bifunctional monomers. This means that this method would be well suited for industrial applications once the authors have proven the experimental validity of this simple, but very innovative, method.

Very recently, Maeda et al. used anionic dipyrrin ditopic ligands (Fig. 7) to obtain neutral DCPs with tetrahedral Zn(II) coordination centers after complexation with Zn(II) ions. They investigated the influence of the spacer between the two dipyrrin moieties of their ligands on the nanoscale morphology of the formed CPs and found, that these CPs are not only fluorescent, but also form nanoscale objects of different shapes depending not only on the ligand conformation but also on solvent conditions [50].

The authors observed nanoscale objects by scanning electron microscopy (SEM), their shape varying with solvent conditions. From THF, at an initial concentration of 10^{-3} M, $\mathbf{1}\cdot\mathrm{Zn^{II}}$ and $\mathbf{4}\cdot\mathrm{Zn^{II}}$ form only randomly shaped objects, whereas $\mathbf{2}\cdot\mathrm{Zn^{II}}$ and $\mathbf{3}\cdot\mathrm{Zn^{II}}$ give uniform nanosized spherical structures of ∼0.3 μm in diameter. In addition, "trains of spheres" are observed in the case of $\mathbf{2}\cdot\mathrm{Zn^{II}}$. When the same system is studied in solution by means of dynamic light scattering (DLS), the diameter in solution is found to be 0.1 μm. To exclude the formation of distinctly shaped objects derived from the ligand on its own, metal-free **1–4** were also studied. However, without metal ion, only amorphous objects form from THF solutions. When the solvent is changed to THF/water (2:1, v/v), hemispheres are found in the cases of $\mathbf{2}\cdot\mathrm{Zn^{II}}$ and $\mathbf{3}\cdot\mathrm{Zn^{II}}$. The latter also creates bell-shaped objects (Fig. 8).

Astonishingly, from this solvent composition $\mathbf{4}\cdot\mathrm{Zn^{II}}$ forms spheres with "craters" instead of amorphous objects. When the water fraction is increased to 50%, only $\mathbf{4}\cdot\mathrm{Zn^{II}}$ still forms well-defined nano-objects, specifically nanosized golfballs. When transferred to CH_3CN, all four compounds form aggregates of smaller spherical objects of ∼100 nm in size. The authors compare the formation of nanoscale objects under these solvent conditions with protein folding as a stepwise process. First, the coordination oligomers must form and then stacking occurs in a secondary step. Stacking is then followed by the formation of spheres, the tertiary step, that then finally assemble into larger objects in the quaternary step. A similar concept was recently published by Mirkin. Controlled precipitation of a coordination polymer resulted in formation of well-defined colloidal particles with potential applications in catalysis [62].

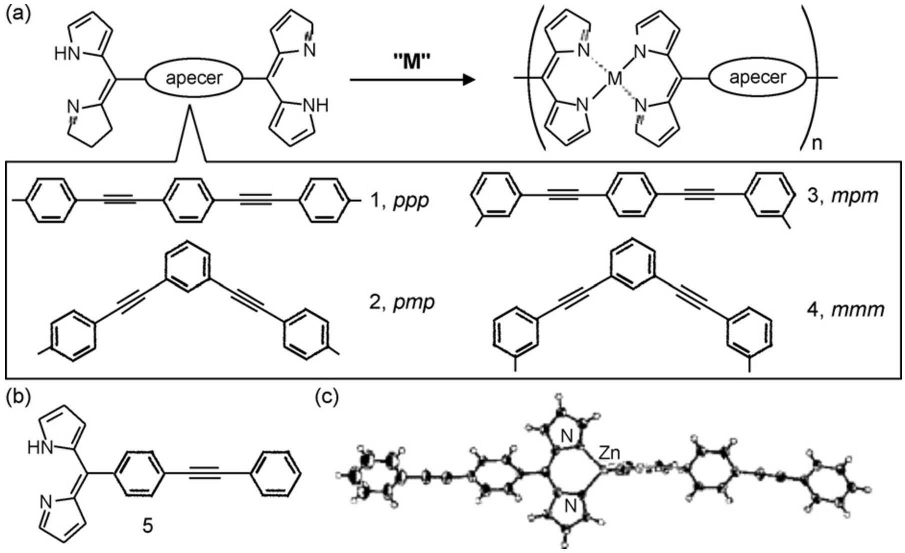

Fig. 7. (a) Metal complexation of dipyrrin "dimers" **1–4**, (b) structure of dipyrrin **5**, and (c) X-ray single-crystal structure of $\mathbf{5}\cdot\mathrm{Zn^{II}}$ as one of its disordered conformations. Thermal ellipsoids are scaled to the 50% probability level [50].

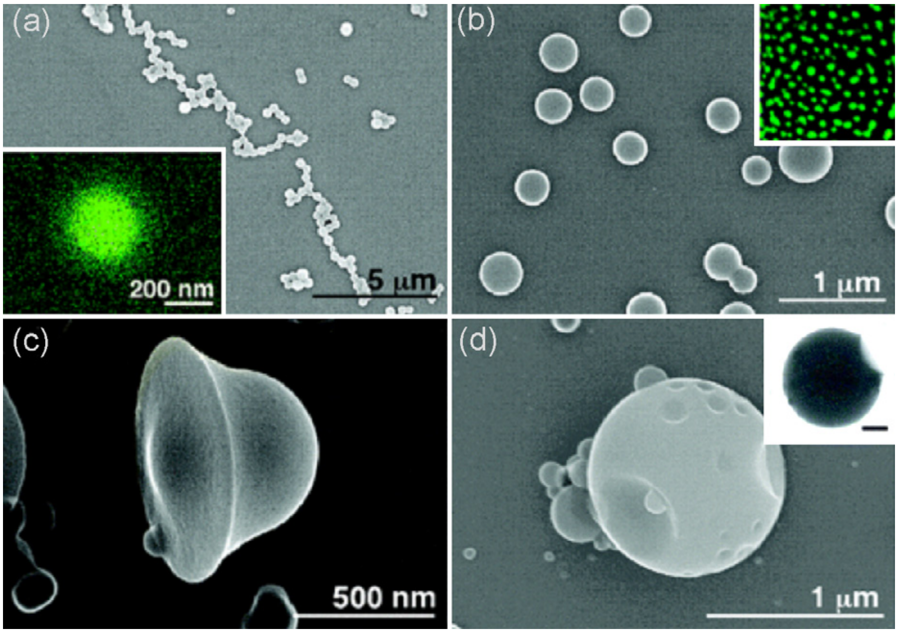

Fig. 8. SEM of (a) **2**·Zn^{II} from THF (8×10^{-4} M; inset: Zn mapping by HRTEM-EDX); (b) **3**·Zn^{II} from THF (3×10^{-3} M; inset: fluorescence micrograph with 25 μm sides of each square); (c) **3**·Zn^{II} from THF/H_2O (2:1, 1.5×10^{-3} M); (d) **4**·Zn^{II} from THF/H_2O (1:1, 1.5×10^{-3} M; inset: TEM with 200 nm bar) [50].

Gerhardt et al. obtained a supramolecular cruciform coordination polymer by the self-assembly of a pyridyl cruciform with a palladium pincer complex. These so-called cruciforms are cross-conjugated 1,4-distyryl-2,5-bisarylethynylbenzene molecules. They are fluorescent compounds and are exhibiting a spatially orthogonal HOMO–LUMO arrangement (Fig. 9).

These rigid compounds can be assembled into ordered monolayer films. Because they possess a high degree of conjugation, they are ideal candidates for advanced electronic and photonic applications, including LED's, LCD's, thin film transistors and optical storage devices [52]. The introduction of electron-donating or accepting groups at the 4′-position of the terminus leads to discrete 2D π-chromophores. This results in an orthogonal HOMO–LUMO arrangement where the HOMO is lying around the axis carrying the electron donating substituents, whereas the LUMO is localized around the axis bearing the electron deficient ones. The aforementioned electronic as well as optical and redox properties can be tuned by varying these donor/acceptor substituents [52]. The authors chose Pd–pincer complexes as ditopic molecular building blocks, since the coordination strength of these compounds can be tuned according to the class of ligand used (nitriles < pyridines < thioureas < phosphines) [53]. The authors exploited this dependency later on to prove the reversibility of their system by substituting the cruciform by a stronger ligand (PPh_3). The complexation as well as the ligand replacement were monitored by UV–vis spectroscopy. The fluorescent cruciform self-assembles with the bis-Pd–pincer complex into a new supramolecular material; the complex formation is accompanied by a bathochromic shift from 445 to 515 nm (Fig. 10), that is reversible upon addition of the stronger PPh3 ligand.

To demonstrate the dependency of the degree of polymerization on stoichiometry, viscosimetric measurements of solutions at different ligand to metal ratios have been carried out, showing a maximum for the relative viscosity at a 1:1 stoichiometry (Table 1). Excess of either ligand or pincer complex leads to a decrease in viscosity, e.g. in chain length.

It has already been shown in previous publications that varying the donor/acceptor substituents tunes the cruciform's optical

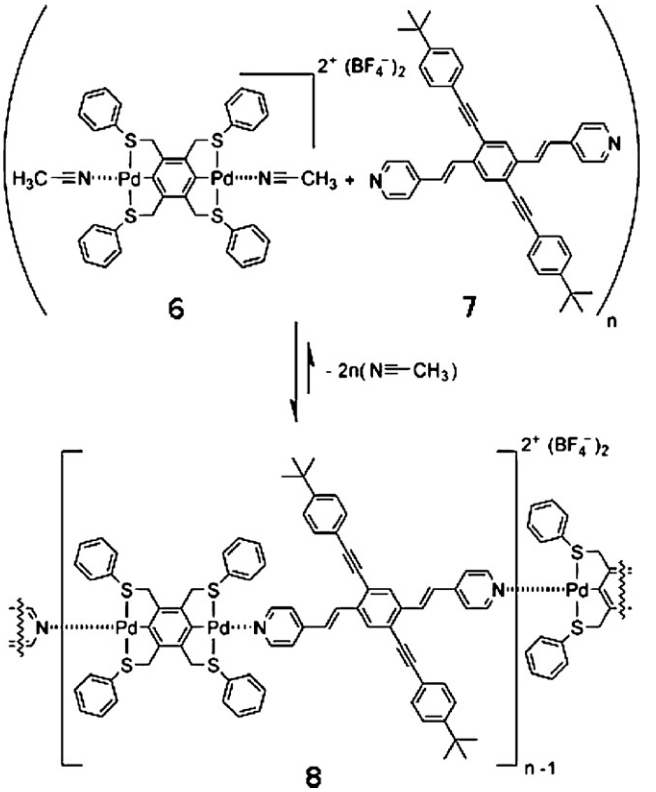

Fig. 9. Supramolecular complex **7**, based on cruciform **6**, self-assembled with bis-pincer complex **5** in a 1:1 molar ratio [51].

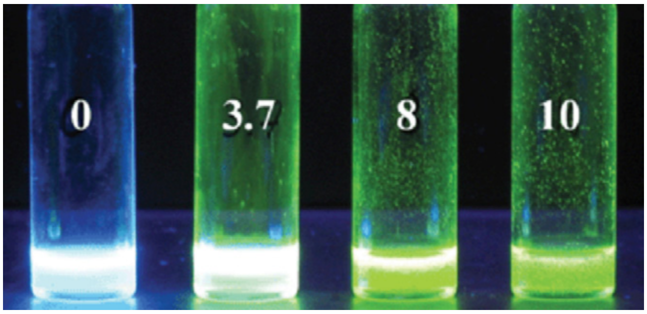

Fig. 10. Emission upon the addition of bis-pincer complex **6** (0, 3.7, 8 and 10 equiv.) to cruciform **7** in $CHCl_3$ under illumination at 365 nm (from Ref. [51]).

Table 1
Relative viscosities of varying ratios of **7** to **6** [51]

Ratio of 7:6[a]	Relative viscosity[b]
0:0	1
0:1	Insoluble
1:2	1.25
1:1	2.83
2:1	1.33
5:1	1.19
1:0	1.09

[a] Total concentration is 0.33 M in 1 ml DMF.
[b] Standardized to 1 ml DMF in an Ubbelohde semi-micro-viscometer.

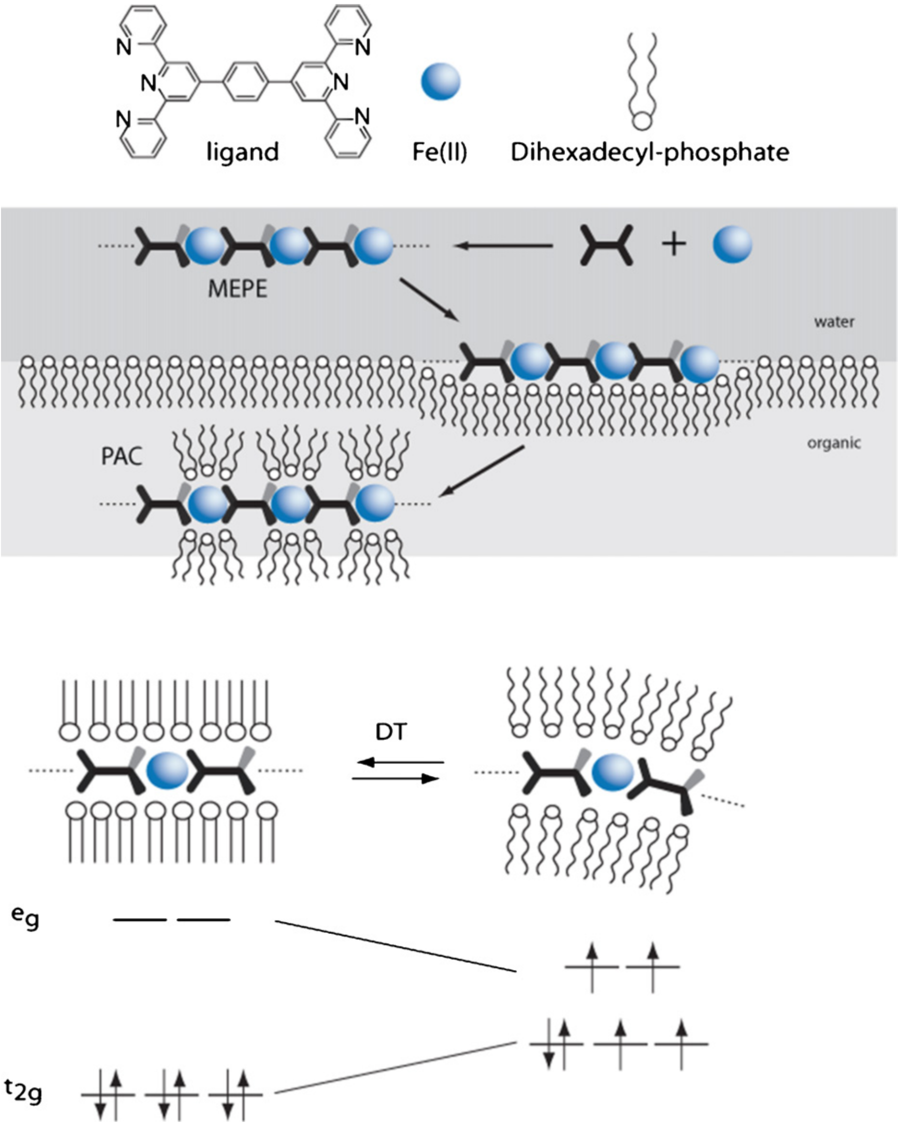

Fig. 11. (Top) Self-assembly of the ditopic ligand and $Fe(OAc)_2$ results in the formation of the linear, rigid-rod-type metallo-supramolecular polyelectrolyte (MEPE). In a consecutive step, MEPE is assembled with dihexadecyl phosphate, resulting in formation of the corresponding polyelectrolyte amphiphile complex (PAC). The amphiphiles render the MEPEs soluble in organic solvents [56]. Spreading PAC at the air–water interface and subsequent transfer of the Langmuir monolayers on a solid support results in a well-defined multilayer, a section of which is schematically shown in the bottom of the scheme. (Bottom) Upon heating of the multilayer, the alkyl chains of the mesophase melt, resulting in a distortion of the metal ion coordination geometry. The unfavorable coordination of the terpyridines around the Fe(II) cation results in a lowering of the energy gap between the d-orbital subset, giving rise to a reversible transition from a diamagnetic low-spin state to a paramagnetic high-spin state [57].

properties [52]. Together with the control over the polymerization degree, this permits the directional design of coordination polymers with specific photophysical properties.

4. Potential for applications in materials science

The idea to use single molecules or molecular assemblies as electronic devices is a very tempting one with probably the most popular example being the molecular switch [54]. In order for a molecular switch to work, a bistable system is needed, meaning a molecular system that is able to switch reversibly (and detectable) from one stable state to another in response to external stimuli. In addition, the system also must be controllable and readable on the molecular level to provide a useful switch. The spin cross-over phenomenon is quite popular in this regard as it is a good example of bistability and is observed in solution as well as in the solid state [55]. For first row transition metals having the d^4–d^7 configuration, there are two possible ground state configurations with different multiplicities: the low-spin (LS) state in which the field splitting parameter Δ between the t_{2g} and e_g sets of the d-orbitals is higher than the spin-pairing energy and the opposite case that gives rise to the high-spin (HS) state. When the spin-pairing energy is in the same range as Δ, the two states can interconvert after being triggered by an external stimulus such as T, p or λ. Such a spin transition is accompanied by pronounced changes of the systems' physical properties (e.g. spectroscopic: colour change; magnetic: diamagnetic (LS) ↔ paramagnetic (HS)). This implies that the spin transition is detectable and can be followed with spectroscopic methods (for example UV–vis spectroscopy, as the spin transition is accompanied by a colour change) or magnetic susceptibility measurements. In addition, the spin transition results in a structural change: a spin transition can be regarded as a $t_{2g} \leftrightarrow e_g$ charge transfer, which implies changes in the population of these orbitals and hence in the metal–ligand bond length.

A remarkable example for this kind of system is the spin cross-over induced by an amphiphilic phase transition introduced by Kurth and co-workers in 2005. They investigated a $Fe^{(II)}$ terpyridine coordination polymer whose counterions were replaced by charged amphiphiles (Fig. 11). In this case, it was not primarily the spin transition that results in structural changes, but a structural change of the amphiphilic matrix, that induced the spin transition.

The magnetic properties of this system were studied in a Langmuir–Blodgett (LB) multilayer, which was obtained by the transfer of Langmuir monolayers onto solid substrates via the LB technique. At the air-water interface, the PAC reorganizes into a bilayer. The amphiphiles, which are not water soluble, form a monolayer at the air interface, while the hydrophilic MEPE is located in the aqueous subphase (Fig. 12). LB transfer of the monolayer on a solid substrate results in a highly ordered multilayer.

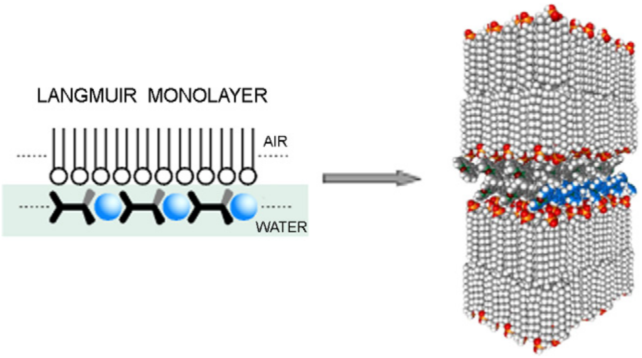

Fig. 12. Left: Structure of PAC at an air-water interface. Right: Molecular model of the resulting LB multilayer. The hydrophobic PAC, which is soluble in common organic solvents, forms Langmuir monolayers at the air-water interface. Transfer of the Langmuir monolayers onto solid substrates via the LB technique permits facile fabrication of metallosupramolecular thin films. In these films, the architecture of the final material, including metal-metal distances, the interlayer spacings, the orientation of each layer as well as the sequence of layers, can be controlled at every step through the used ligands, metal ions, amphiphiles, and transfer conditions.

The entire process evolves through multi-step self-assembly with interactions at several levels and length scales including metal ion coordination, electrostatics, and van der Waals forces. The possibility to make such compounds available in the form of thin layer films is very important for potential applications because this process is readily automated and a large number of different components can be assembled into the layers. Structural studies of this multilayer with X-ray reflectometry revealed a periodicity of 57 Å, which corresponds to flat lying coordination polymer chains and upright-standing amphiphiles. Additionally, extended X-ray absorption fine structure (EXAFS) experiments confirmed that the central metal ion is coordinated to the terpyridine moieties in a pseudo-octahedral coordination environment [58]. Upon heating, the amphiphiles undergo a phase transition, which results in a sufficiently strong mechanical strain to induce a (reversible) spin transition from a LS to an HS state [57]. While an entropic contribution cannot be completely ruled out, the phase transition of the amphiphilic phase is currently believed to be the major contributor to the spin transition.

As it has already been shown that the coordination polymers adsorb to solid supports to form ordered films, it is now important to focus on research that manipulates these system's properties. Interesting in this regard is the work of Sijbesma et al. They investigated the formation of a reversible Pd(II) coordination polymer. They observed reversible ultrasound induced chain scission of the dissolved polymer by dissociation of the phosphane ligands; the original molecular weight was restored after sonication [59]. The system investigated here was built-up from a ditopic phosphane ligand and PdCl2 to form a linear coordination polymer (CP), both shown in Fig. 13 [59].

They showed that no covalent bonds were broken during the sonication process, but that it is selective for the weaker Pd–phosphane coordination bonds. During several sonication-equilibration cycles, the molecular weight of the studied CP decreased during sonication, but was restored almost quantitatively during the equilibration phase (Fig. 14).

Therefore, the sonication of reversible coordination polymers can be used to control ligand exchange to obtain, for example heterocomplexes that are difficult to obtain by other

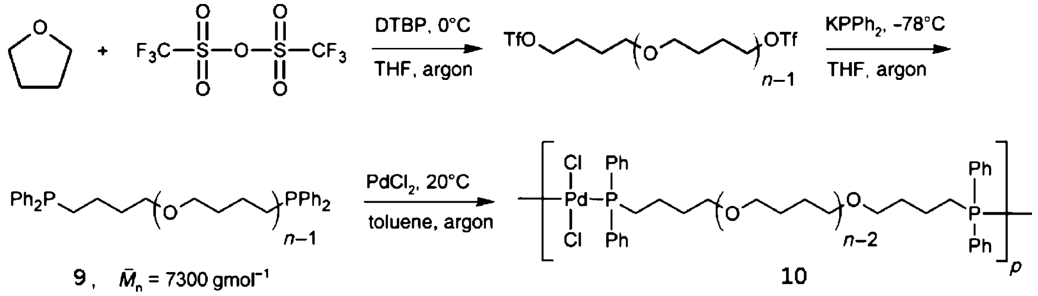

Fig. 13. Synthesis of the polymeric diphosphane ligand and coordination polymer. DTBP: 2,6-di-*tert*-butylpyridine; Tf: trifluoromethanesulfonyl [59].

synthetic methods. However, an issue still to address is an increase in the scission rate. Once this increase is achieved, applications in catalysis can be envisioned that exploit the switchability of the catalytic activity by ultrasound-induced scission of metal–ligand bonds. Another interesting potential application is be the use of coordination polymers as carriers of charged macromolecules which is possible due to their polyelectrolyte character. Much research in the group of Stuart et al. has focused on this subject [60]. Over the last decade, Stuart et al. have investigated a very interesting new class of coordination polymers: the complex coacervation core micelles, named C3Ms. These C3Ms were obtained from a mixture of ditopic ligands, metal-ions and cationic–neutral diblock copolymer in an aqueous solution. In this mixture, the formation of stable and well-defined core-shell nanostructures at their equilibrium position was observed. This growth was based on a hierarchical self-assembly process, that was driven by the electrostatic interactions between the charged polymers. The recognition process on the molecular level requires several different attractive and repulsive interactions to be present in the system. The C3Ms are two component self-assembling colloids that contain a double hydrophilic diblock copolymer and an oppositely charged homopolymer. In the former, one of the blocks is a polyelectrolyte whereas the other one is neutral. When a mixture of polyelectrolytes is close enough to isoelectric conditions, this system can phase separate. In the specific case of a mixture that forms C3Ms, the polyelectrolyte block of the copolymer tends to phase separate together with the oppositely charged polyelectrolyte from the neutral copolymer blocks to form micellar systems. Therefore, the growth of this micellar system is limited by the fact that part of the constituent molecules do not participate in the micelle formation, e.g. the neutral copolymer blocks (Fig. 15).

The driving force for micelle formation is the entropy gain induced by the liberation of smaller counterions initially attached to the polyelectrolytes that counterbalanced their charges. This mechanism implies that the C3M-formation can

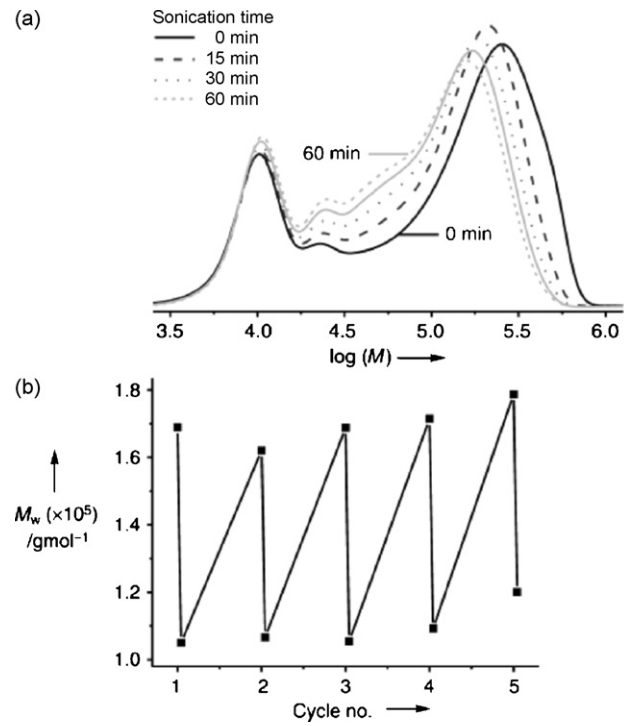

Fig. 14. Ultrasound-induced decrease in the molecular weight of the Pd(II) CP (1.5 mM in toluene): (a) molecular-weight distribution of samples taken during sonication; (b) weight-averaged molecular weight during a reversibility test consisting of five cycles of sonication (1 h) followed by equilibration (23 h) [59].

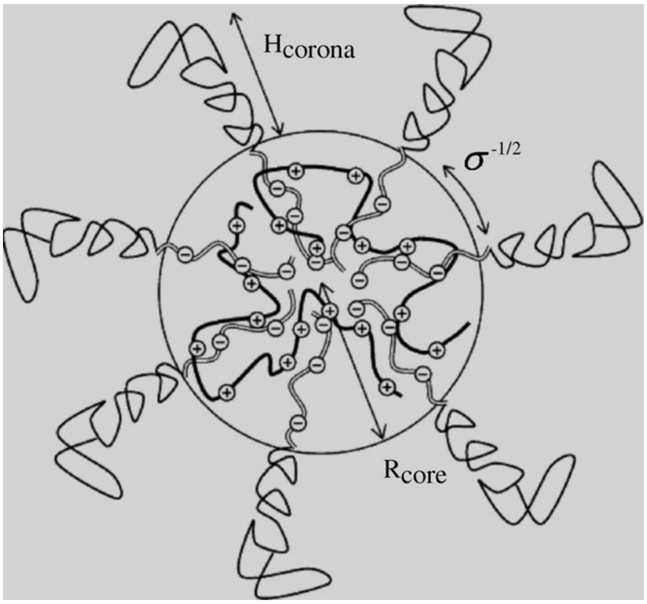

Fig. 15. The thickness of the corona or extension of corona blocks into the bulk solution is represented by H_{corona}. The radius of the core is represented by R_{core}. The total micellar radius is given as $R_{\mathrm{micelle}} = R_{\mathrm{core}} + H_{\mathrm{corona}}$ [61].

be suppressed by high salt concentrations. Stuart et al. have found that the copolymer block ratio is an important parameter in micelle formation: In the case where a 1:1 (charged/uncharged) copolymer was used, a macroscopic phase separation was observed as the length of the neutral block is apparently not sufficient to stop the micelle growth at a certain point. When a 1:3 copolymer was used in the mixture, scattering experiments showed a maximum at the isoelectric composition without any indications for a macroscopic phase separation. This result indicated the formation of well-defined micelles, which was supported by Cryo-TEM analysis of the mixture showing many small dark objects with an estimated size of around 10 nm. However, the formation of these micelles does not appear instantaneously upon mixing of the different components of the system. It is preceded by a macroscopic phase separation into a polymer-rich and a polymer-poor phase of which the former then rearranges into a stable micellar solution. By adding salt in various concentrations, Stuart et al. also found that the micelle formation was reversible at salt concentrations of 0.5 M NaCl and beyond. At these concentrations, the micelles are no longer stable and disappear. C3Ms are interesting compounds due to their potential application as nanoscale carriers in the delivery of charged compounds such as DNA or proteins.

5. Concluding remarks

This review gives an overview of recent advances in the field of transition metal coordination polymers. We intended to give a short classification for coordination polymers as well as an overview of already established and upcoming methods to characterize and manipulate this class of compounds. There is still much work to be done to reach a more complete understanding of these materials. As pointed out in this article, the relation between binding constant, concentration and chain length of a coordination polymer can be exploited to design systems with specific properties. Literature on coordination polymers is increasing rapidly and significant progress in this field can be expected in the near future. In particular, reliable techniques for the characterization of this class of compounds need to be developed and established in order to fully exploit the large potential of these materials. Equally important is that synthetic methods must be further refined in order to produce DCPs in reliable and reproducible ways. Consistent synthesis is critical because the structure and resultant properties depend critically on concentration, stoichiometry and other parameters. Only with standardized synthesis methods will it be possible to obtain comparable and meaningful results. However, once these steps are achieved, the opportunities are endless if we consider the freedom we have in the design of the ligands, the choices of metal ions, counter ions and self-assembly conditions. Possible structures range from linear polymers, which have been mainly studied so far, to all the other known polymer architectures all the way to colloidal systems. Blending dynamic properties, the value-adding features of transition metal ions and self-assembly into polymer science provides an enormous diversity and access to new classes of materials. We therefore confidentially predict that dynamic coordination polymers will have significant impact in research, science and technology.

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