Combination of orthogonal supramolecular interactions in polymeric architectures

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Supramolecular polymers represent a highly interesting approach towards new ''smart materials''. A recent strategy includes the combination of different ''orthogonal'' non-covalent binding sites within one polymer system. Different functionalities can be introduced in a highly defined way by controlled self-assembly processes. This feature article presents highlights in the supramolecular polymer chemistry of multiple hydrogen-bonding, metal complexation (especially of bi- and terpyridines) and host–guest interactions as well as recent advances in combining these interactions in novel polymers.

Introduction

Over the past few years, supramolecular chemistry has evolved to be one of the most interesting fields in modern chemistry. In 1987, J.-M. Lehn, C. J. Pederson and D. J. Cram received the Nobel Prize for their pioneering work.[1] The synthesis of large molecules by traditional covalent chemistry is rather time-consuming and also cost-intensive. On the other hand, nature utilizes a wide range of different non-covalent interactions for the construction of large supramolecular architectures.[2] Non-covalent interactions (intra and intermolecular) are responsible for most biological processes such as highly selective catalytic reactions and information storage.[3] One of the best-known examples is DNA, where the self-recognition of the complementary base-pairs by hydrogen-bonding leads to the self-assembly of the double helix.

Self-recognition and self-assembly processes represent the basic concept of supramolecular chemistry and the involved non-covalent interactions (*e.g.* van der Waals forces, hydrogen-bonding, ionic or coordinative interactions) are usually weaker than covalent bonds. Moreover, supramolecular interactions are reversible, whereas covalent bonds are usually irreversible or only reversible under harsher conditions. Today, a variety of synthetic supramolecular systems are known.[1,4] Such compounds are expected to reveal new chemical, physical as well as biomimetic properties. The concept was recently extended to ''molecular machines'',[5] which could act as the link between micro- (or nano-) technology and molecular chemistry. Finally, supramolecular polymers[4,6,7] are expected to lead to new materials with tunable properties.

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Orthogonal supramolecular bonding

Biomolecules are characterized by a combination of different supramolecular interactions. These non-covalent binding sites are highly selective: the principle of ''orthogonal supramolecular interactions'' describes non-covalent interactions that do not interfere with each other directly. Multifunctionality is the basic characteristic of biological systems. In proteins, for example, the ensemble of various supramolecular bonds is responsible for their specific structure and provides centers for catalytic biochemical reactions.

In the protein haemoglobin, for example, all kinds of supramolecular interactions including metal coordination are present in the same molecule and are responsible for the structure and properties (Fig. 1). The main task of the porphyrin–metal complexes (Haem-groups) is the transportation of O_2 in the metabolic process: an oxygen molecule binds

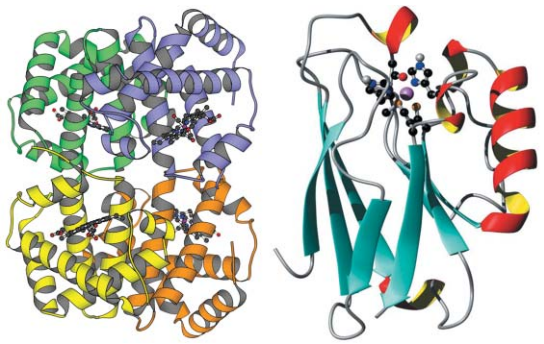


Fig. 1 Model of haemoglobin[8] and azurin (reproduced from ref. 9)

to the vacant coordination site on the metal center and is released when it is needed.

Another example is ATP-synthase. This enzyme is actually a "molecular machine" and non-covalent interactions are responsible for many tasks such as binding the protein to the cell membrane, transporting protons through the membrane and the synthesis of ATP from ADP molecules.[10] Also azurin can be mentioned in this context. This protein, which catalyzes redox reactions in organisms, is widely studied as a model electron-transfer protein and contains all supramolecular interactions from hydrophobic and hydrophilic interactions *via* hydrogen-bonding to metal coordination (copper complex).[11]

In contrast to biological systems, synthetic supramolecular chemistry usually utilizes only one type of interaction at a time. Various examples where hydrogen-bonding, π-stacking or metal coordination is employed are known.[4,7,12] Among the most famous moieties in this respect are ureidopyrimidinone as a hydrogen-bonding unit and terpyridine as a metal chelator (Fig. 2). However, the introduction of different supramolecular functional groups (multifunctionalization) into one synthetic entity would drastically improve the possibilities for application of such materials. "Orthogonal" self-assembly (that means the supramolecular binding units need to be selective and must not interfere with each other) would allow full control over the self-assembly step and therefore the materials' properties. Applications as biosensors or in drug delivery as well as catalytic processes could be achieved.

In this feature article, highlights of the chemistry of supramolecular polymers containing hydrogen-bonding, metal coordination and host–guest interactions as well as the various architectures obtained will be presented, followed by selected examples where several of these interactions were combined within one functional polymer system.

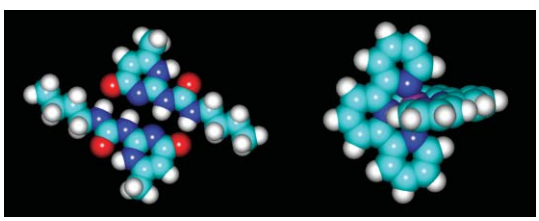
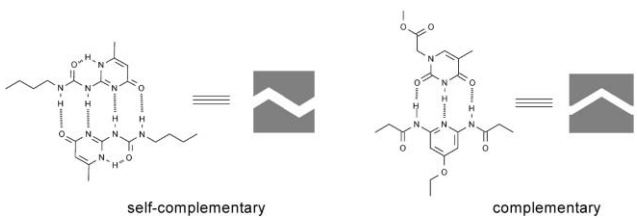


Fig. 2 Representation (molecular modeling) of the ureidopyrimidinone dimer (left) and a terpyridine metal complex (right) (HyperChem).

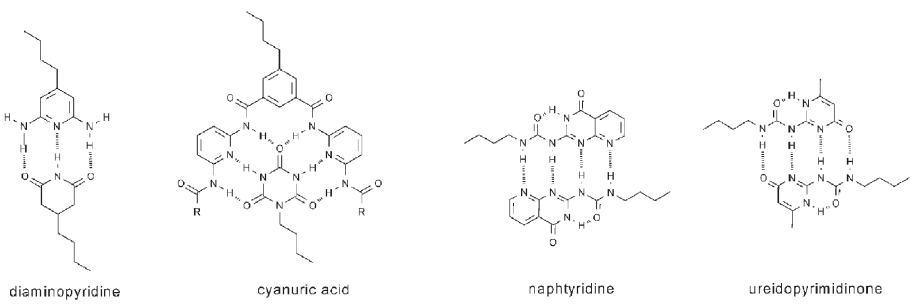
Hydrogen-bonding

In polymer chemistry, numerous attempts have been undertaken to exploit hydrogen-bonding for the synthesis of new materials. Multiple hydrogen-bonding is of major importance since the obtained aggregates are of enhanced stability compared to single hydrogen-bonding. In DNA, for example, dual respective triple hydrogen-bonds are formed between the base-pairs. Scheme 1 shows some typical hydrogen-bonding motifs used for supramolecular polymers.

There are two main types of multiple hydrogen-bonding systems: complementary and self-complementary units (Scheme 2). In complementary systems (*e.g.* maleimide and 2,4-diamino-6-vinyl-1,3,5-triazine, forming triple hydrogen-bonds[13]), both complements must be present to establish the hydrogen-bonds through self-recognition, whereas in self-complementary systems the hydrogen-bonds are automatically formed between the units as soon as the conditions (*e.g.* the solvent used) allow. In the bulk, the hydrogen-bonds are also present. Ureidopyrimidinone is a self-complementary hydrogen-bonding unit, containing a donor–donor–acceptor–acceptor (DDAA) array of hydrogen-bonding sites.[14] The



Scheme 2 Schematic representation of self-complementary (left) and complementary (right) multiple hydrogen-bonding.



Scheme 1 Schematic representation of well-known multiple hydrogen-bonding moieties.

resulting aggregate allows additional secondary attractive interactions between the neighboring hydrogen-bonds, resulting in a high association constant ($K_a = 6 \times 10^7$ M^{-1} in chloroform).[14,15]

Linear polymers

In the group of Meijer, the strong self-complementary hydrogen-bonding of ureidopyrimidinones[14] has been extensively used for the assembly of linear supramolecular polymers (Fig. 3).[6] For this purpose, organic bis-ureidopyrimidinones[16] as well as polymeric[17,18] telechelics have been applied. Dynamic systems with a strong dependence of the molecular weight on concentration are the result. The formation of high molecular weight species was shown by viscosimetry, which revealed an exponential relationship of the viscosity with concentration.[16] Improved material properties were demonstrated with rheometry and dynamic mechanical thermal analysis (DMTA).[18] In the case of small organic telechelics, the tendency for the formation of small rings or polymeric species is strongly dependant on the constitution of the spacer:[19,20] Linkers containing specific side groups lead to a conformation favoring ring-formation. In the laboratories of Guan, ureidopyrimidinones were used for the preparation of biomimetic polymers: the moieties were incorporated within the main chain of the polymer, resulting in "loops" through intramolecular hydrogen-bonding (Fig. 4).[21] Such polymers are expected to reveal an increased mechanical strength while possessing high elasticity. This concept was extended to polymers containing peptidomimetic β-sheet motifs and monodisperse loops.[22]

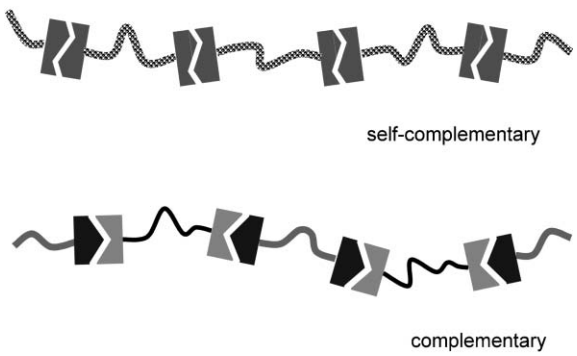


Fig. 3 Schematic representation of linear supramolecular polymers formed by self-complementary and complementary hydrogen-bonding units.[6,16,18,20]

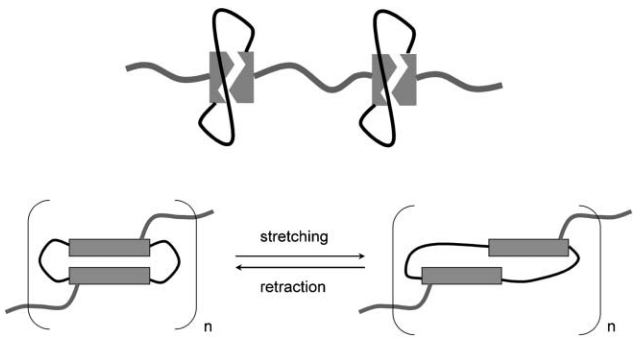


Fig. 4 Schematic representation of biomimetic polymers containing intramolecular hydrogen-bonding.

Complementary hydrogen-bonding units have also been employed for the synthesis of linear supramolecular polymers. In the group of Lehn, sextuple hydrogen-bonds of diaminopyridine-substituted isophthalamide and cyanuric acid were employed to form supramolecular polymers.[23] In such systems, the molecular weight can easily be adjusted by the stoichiometry of the two components.

Grafted architectures

Rotello *et al.* reported the construction of side-chain functionalized polystyrenes bearing diaminotriazine or diaminopyridine[24] moieties. These hydrogen-bonding units represent a D–A–D motive that is not self-complementary. Subsequent addition of suitable compounds containing an A–D–A recognition unit resulted in reversible side-chain modification (Fig. 5). In these so-called "plug and play" polymers, small organic guest molecules (flavin) were connected to the polymers and the complexation monitored by measuring the fluorescence quenching of the flavin unit. The diaminotriazine polymer was found to form micelle-like aggregates through intramolecular hydrogen-bonding,[25] making the hydrogen-bonding unit less accessible for guest-binding.

In a more recent publication,[26] the thymine group (A–D–A motive) was connected to the polymer, and silsesquioxane groups were connected to the backbone by hydrogen-bonding, representing an approach to organic–inorganic hybrid materials. The grafting approach was also used by Ober *et al.* Mesogenes bearing an imidazole end-group were connected to a polystyrene-block-poly(acrylic acid) through single hydrogen-bonding and were subsequently aligned in an electric field to form a liquid-crystalline phase.[27]

Networks through hydrogen-bonding

Hydrogen-bonding interactions are a well-suited tool for the preparation of reversible polymer networks (Fig. 6). These systems could find applications, *e.g.* in the field of smart materials as self-healing coatings. An early example of networks was reported by Stadler *et al.*: by modifying a poly(phenylene) with 1,2,4-triazoline-3,5-diones, an increase of viscosity was found with increasing substitution.[28] The same group reported also poly(butadienes) modified with hydrogen-bonding moieties, which lead to thermoplastic elastomers.[29] Another example of cross-linking by hydrogen-bonding describes a blending of a tetrakis-pyridine and a bis-carboxylic

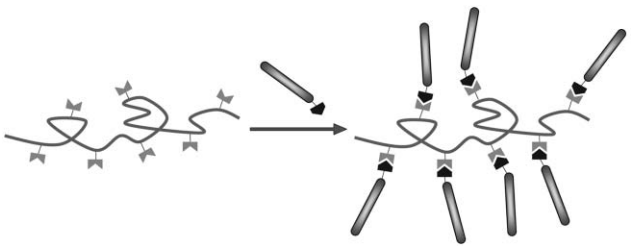


Fig. 5 The "plug and play" approach of Rotello *et al.*[24,26]

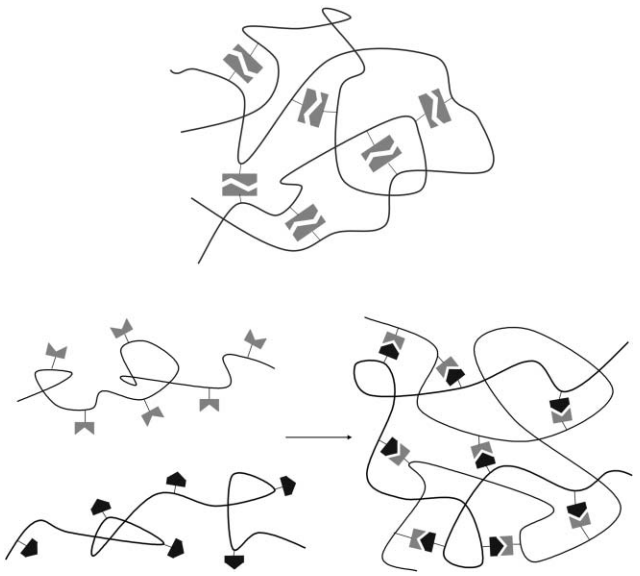


Fig. 6 Top: hydrogen-bonding networks by self-complementary hydrogen-bonds.[32] Bottom: cross-linking by blending two polymers containing complementary hydrogen-bonding units.[13]

acid.[30] A different approach consisted of 3-amino-1,2,4-triazole units in the side-chain of the polymer, resulting in a thermoreversible supramolecular rubber.[31] In the examples of Rieth *et al.* ureidopyrimidinone moieties were introduced into the side-chain of a copolymer (Fig. 6, top).[32] Also in the groups of Long and Meijer, polymers bearing ureidopyrimidinone in the side-chain were prepared.[33,34]

Another possibility for cross-linking by hydrogen-bonding includes complementary hydrogen-bonding (Fig. 6, bottom).[13] In this case, the cross-links are established by blending two polymers containing the respective functional groups. The cross-linking density could be easily adjusted by changing the ratio of the components, making fine-tuning a possibility.

The polymers prepared by Rotello *et al.* (also see above) revealed an interesting feature: a diaminopyridine functionalized polymer formed micrometre-sized aggregates in apolar solvents (microspheres) by cross-linking *via* self-complementary double hydrogen-bonds. After addition of a thymine-functionalized polymer, the structure of the aggregates changed to vesicles containing complementary triple hydrogen-bonds. The size of the aggregates could be controlled by the molecular weight of the polymer and the transition is reversible; adding diaminopyridine-polymer to the vesicles converted them back to the microspheres.[35]

Metal complexation

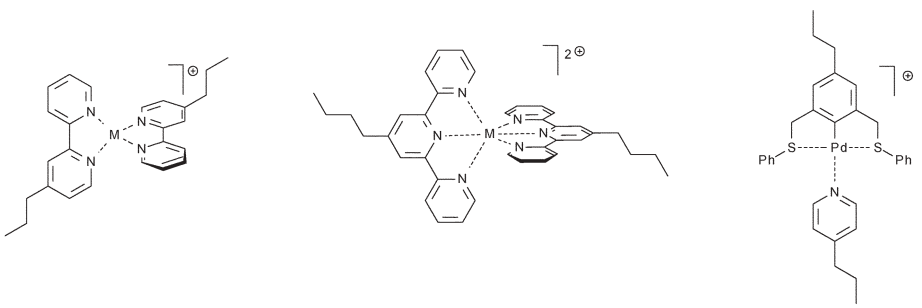
Metal coordination of chelate complexes has been extensively exploited for the construction of supramolecular architectures. The most prominent examples are bipyridines and terpyridines, but also palladated pincers are used (Scheme 3).

Metal complexes of bi- and terpyridines[7,36] are of special interest, because these complexes allow the reversible formation and cleavage of the metal coordinative bond by external stimuli, *e.g.* redox processes or the addition of competing ligands.[37,38] Terpyridine ligands are among the most versatile systems since they allow the defined construction of a variety of defined supramolecular architectures and polymers. Opposed to tris-bipyridine metal complexes, no isomers are formed for 4′-functionalized bis-terpyridine complexes. Moreover, the supramolecular link can be tuned by the metal ion used. Whereas zinc(II) forms labile, reversible complexes, the corresponding iron(II) or ruthenium(II) complexes are very stable and rather inert. Several reviews have been published over the past few years on this topic.[7,39,40] Moreover, the ruthenium(III)/(II) chemistry[41] allows the preparation of symmetric as well as asymmetric complexes (Scheme 4). Therefore, the terpyridine can act as a self-complementary as well as a complementary recognition unit, only dependent on the type of complexation procedure utilized.

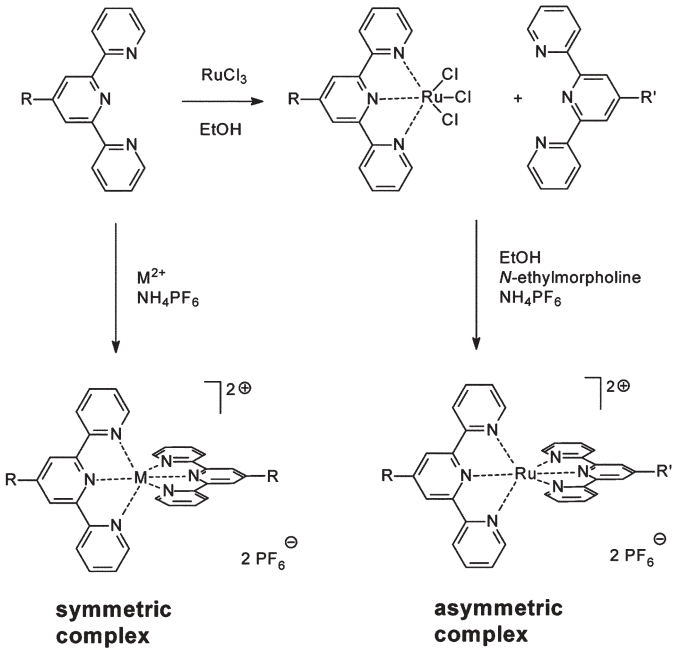
Linear metallopolymers

The directed synthesis of asymmetric terpyridine–ruthenium complexes is a valuable tool for the preparation of block copolymers (Scheme 5). Like in a LEGO® system, various building blocks can be combined,[42] allowing also the construction of block copolymer libraries.[43]

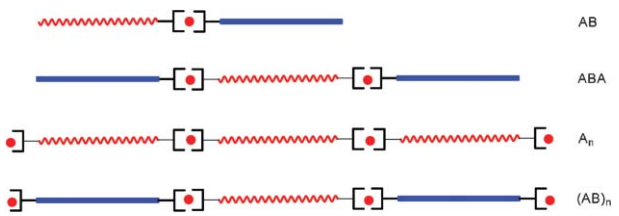
Among the prominent examples are amphiphilic supramolecular block copolymers, consisting of a water-soluble poly(ethylene glycol) and a hydrophobic polystyrene or poly(ethylene butylene) block. By changing from DMF as a good solvent for both polymer entities to water as a selective solvent for the poly(ethylene glycol) blocks, spherical micelles were obtained and imaged by transmission electron microscopy.[37,44] These micelles could be stripped off their corona by applying a competing ligand to open the terpyridine complexes.[37] Significant differences to their covalent analogues were found (shrinkage through salt-addition), and the



Scheme 3 Schematic representation of well-known metal complexes based on chelating ligands.



Scheme 4 Approaches to symmetric and asymmetric terpyridine metal complexes.



Scheme 5 Various accessible architectures of linear metallopolymers.

terpyridine ruthenium(II) complexes are believed to be at the interface between the shell and the corona.[45]

Precursors containing two terpyridine moieties have been employed to construct extended linear coordination polymers. In the laboratories of Rehahn, *p*-bis(terpyridine) functionalized phenyl compounds were utilized to prepare rod-like coordination polymers.[36]

Flexible telechelics were also successfully utilized. Oligomeric and polymeric ethylene glycols could be functionalized with terpyridine moieties and subsequently converted into linear metallo-supramolecular architectures of high molecular weights (Fig. 7).[38,46,47] Recently, even automated synthesis using a combinatorial approach was achieved successfully, allowing the preparation of libraries of supramolecular polymers.[48]

Grafting and cross-linking through complexation

Cross-linking. Metal complexation could be employed for the cross-linking of polymers bearing multiple metal-complexing units. The first examples have already been reported in the

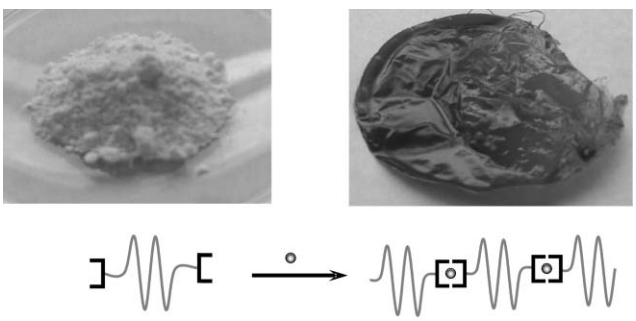


Fig. 7 Film formation after complexation of a polymeric bis-terpyridine (ruthenium(II)).

1990s.[28,49,50] Through the complexation of bipyridine moieties, redox and thermoreversible hydrogels were obtained. By connecting a polymerizable group to terpyridine ligands, copolymers bearing pendant terpyridine moieties were synthesized by random copolymerization.[51,52] Recently, copolymers of this type could also be prepared in a controlled fashion: applying reversible addition–fragmentation chain transfer polymerization (RAFT), random as well as block architectures were constructed.[53] The addition of metal ions to such a copolymer leads to cross-linking through complex formation (Fig. 8, right).

The addition of iron(II) and zinc(II) ions to terpyridine-containing copolymers in diluted solution resulted in drastically increased viscosities, showing the formation of cross-linked aggregates (due to the low concentration used no precipitation was observed).[54] The viscosity was dependant on the terpyridine content in the copolymer and the nature of the

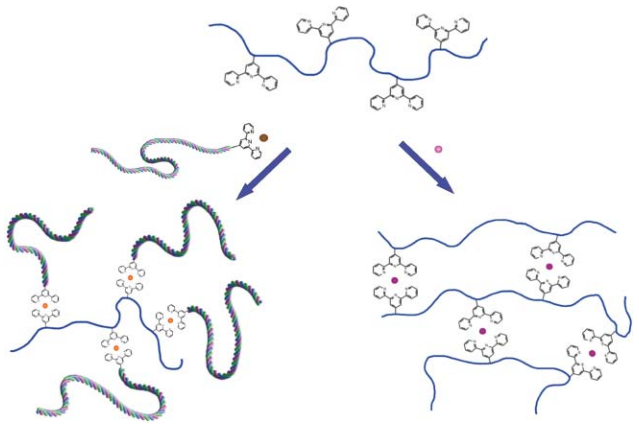
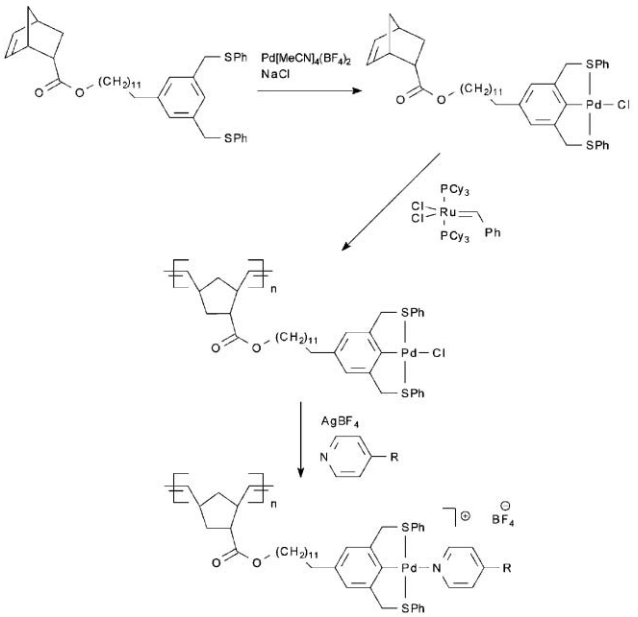


Fig. 8 Grafting and cross-linking of a copolymer containing terpyridine moieties in the side-chains.

utilized metal ion. The weaker and reversible zinc(II) complexes revealed a lower viscosity than the analogous iron(II) systems, indicating the formation of smaller aggregates. At higher concentrations, gel formation was observed.[55]

2,6-Bis-(1′-methylbenzimidazolyl)pyridine is another tridentate ligand that could be employed for the construction of metallo-supramolecular polymers. Besides bis-complexes with transition metal ions, stable tris-complexes could also be formed with lanthanide ions. Therefore, linear as well as cross-linked systems could be prepared using one ligand. Moreover, this strategy allows adjusting the cross-linking density by adjusting the ratio of bis-coordinating and tris-coordinating metal ions. Reversible thermo-responsive and mechanic-responsive (thixotropic) gels were obtained.[56]

Grafting. The directed complexation to asymmetric terpyridine complexes utilizing the ruthenium(III)/(II) chemistry allows the side-chain terpyridine-functionalized copolymer to be modified in a grafting approach.[57] Ruthenium(III) monocomplexes of terpyridines bearing polymeric and non-polymeric functionalities were attached to a terpyridine-containing backbone (PMMA) in a polymer-analogous manner (Fig. 8, left). Among the reported examples is an amphiphilic graft copolymer, where poly(ethylene glycol) chains were connected to the poly(methyl methacrylate) backbone. Spherical aqueous micelles could be obtained by changing the solvent from DMF to water. As expected, the so-prepared micelles were more polydisperse than the corresponding block copolymer micelles.[58] In a different approach, pre-formed ruthenium(II) complexes containing a polymerizable group (styryl) were copolymerized with styrene.[59] Yet another method consists of the polymer-analogous modification of PVC with terpyridine moieties and the subsequent grafting and cross-linking of the pending ligand units.[60] In the laboratories of Weck, poly(norbornenes) containing palladated pincers, were prepared (Scheme 6).[61] A norbornene was functionalized with a phenyl ring bearing two sulfide groups, representing a sulfur–carbon–sulfur pincer ligand that was subsequently complexed with a PdCl-fragment. The norbornene moiety was polymerized by ring-opening methathesis polymerization (ROMP). Finally, the chloride of



Scheme 6 Schematic representation of the preparation of polymers containing palladated pincers by ROMP methodology.

the palladated pincer could be substituted by various functionalized pyridines, making such complexes interesting as building blocks for functional polymers. Moreover, complexes of this type were shown to possess catalytic activities.[62]

Host–guest interactions and biological systems

Finally, host–guest interactions play an important role in the construction of supramolecular architectures: these non-covalent interactions can be very strong and specific. Calixarenes are known to encapsulate small guests like benzene. If bis-calixarenes are employed, linear supramolecular polymers are obtained (Fig. 9a).[63] In addition to hydrophobic and aromatic host–guest interactions, hydrogen-bonding of the urea groups at the rim lead to stable aggregates. Another contribution describes a copolymer containing recognition units for cyclodextrins (adamantane or *p*-(*tert*-butyl)phenyl groups) in the side-chain.[64] The cyclodextrin moieties could be modified with dodecyl chains, resulting in vesicles, which could be subsequently coated with the copolymer bearing the guest unit (Fig. 9b). The binding of the copolymer to the vesicles was found to be stronger compared to single cyclodextrins, as a result of multiple host–guest interactions.

One of the strongest non-covalent interactions known in the field of host–guest systems is biotin–avidin, where the biotin moiety fits like a key into the "lock" of the protein. A combination of hydrophobic and hydrogen-bonding interactions results in aggregates with an association constant of 10^{15} mol^{-1}. The immobilization of biotin to surfaces or polymer matrices could lead to potential applications, *e.g.* as biosensors. One recent example describes the preparation of a poly(L-lysine)-g-poly(ethylene oxide) that was modified with biotin.[65] This polymer adsorbs to negatively charged surfaces,

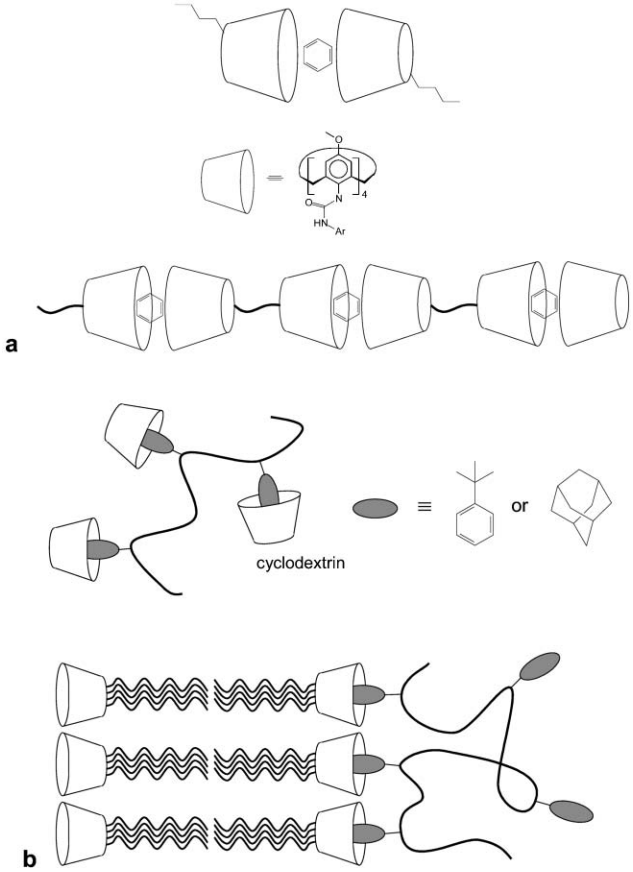


Fig. 9 Supramolecular polymers through encapsulation of calixarenes.

resulting in biotin-coated surfaces that bind, *via* avidin, *e.g.* antibodies (Fig. 10).

Combination of different supramolecular systems

Polymers bearing functional groups play an important role in the design of new materials such as organic solar cells, LEDs or smart materials with self-healing properties. A very versatile approach is the linkage of the functionalities to a polymer backbone *via* self-assembly processes. Certain functional materials require the presence of two different functional moieties (*e.g.* donor and acceptor), which have to be introduced in a defined and controlled manner. If only one kind of supramolecular recognition unit (anchor) is present in a polymer backbone, statistical mixtures are usually obtained, when two or more functional units are applied (Fig. 11, top). Therefore, control of the self-assembly reaction is limited and the product is ill-defined. The combination of different (orthogonal) supramolecular binding units, however, allows control of the self-assembly step (Fig. 11, bottom). Well-defined multifunctionalization of polymers can be achieved if a high selectivity of the orthogonal recognition units to their complementary counterparts exists. Two different pathways are imaginable for multiple self-assembly. *Via* sequential self-assembly, one functionality can be introduced first, followed by the second one. However, a one-pot approach also leads to the defined multifunctionalized product, making one reaction step obsolete.

This strategy of controlled multifunctionalization allows the fine-tuning of polymer architectures as well as properties, and opens avenues towards new tailor-made functional materials. A very facile and versatile approach to such materials is based on terpolymers bearing different recognition units in the side-chain. These polymers are easily available by terpolymerization of common monomers (*e.g.* (meth)acrylate or styrene) together with functionalized monomers.

Hydrogen-bonding and metal complexation

In the group of Weck, copolymers bearing hydrogen-bonding moieties as well as metal complex units (palladated pincers) in the side-chain, were prepared (Fig. 12). Poly(norbonene) was

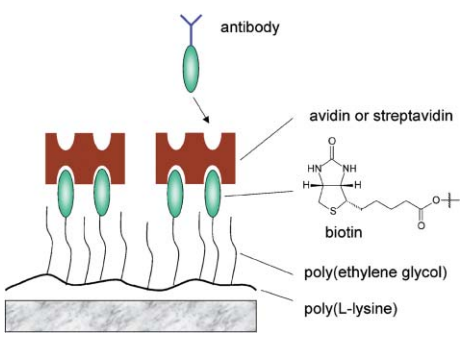


Fig. 10 Concept of a biosensor *via* a biotin-modified polymer immobilized on a surface.

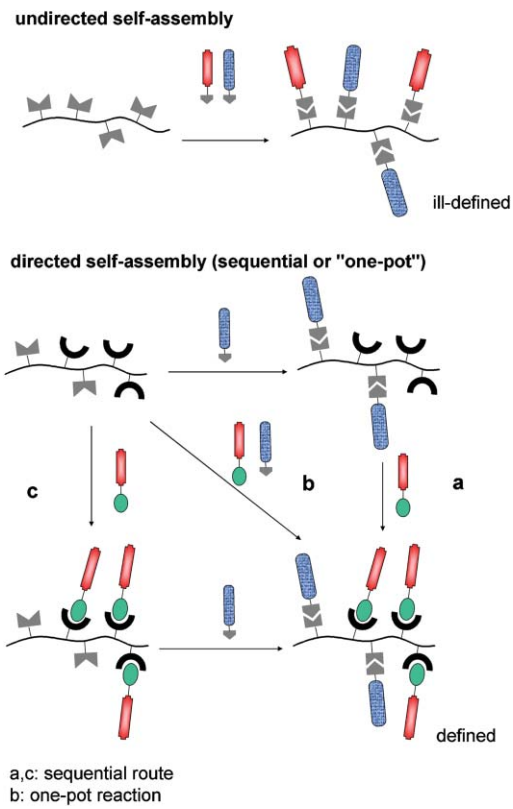


Fig. 11 Statistical (top) and defined (bottom) multifunctionalization of a polymer by self-assembly.

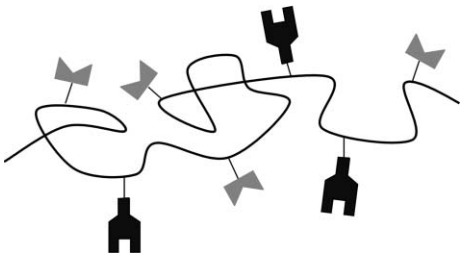


Fig. 12 Schematic representation of a terpolymer containing hydrogen-bonding and metal coordination sites (pincer ligands).

chosen as the backbone system. The polymers were obtained by ring-opening metathesis polymerization of norbornene together with the corresponding functionalized norbonenes.[66–68] ROMP is a living polymerization technique, which is tolerant to a variety of functional groups. Moreover, the resulting polymers are high-grade materials that find applications in high-impact corrosion resistant materials or dental products.

A recent contribution describes the preparation of a random copolymer bearing hydrogen-bonding moieties based on diaminopyridine (not self-complementary) and palladated pincers as metal coordinating groups.[69,70] This polymer was obtained by ROMP and it could be functionalized either sequentially or in a one-step ''orthogonal'' self-assembly, leading to the same product. The hydrogen-bonding moiety was functionalized with *N*-butylthymine and pyridine was used as the ligand for the complexation of the palladated pincer as a model system.

Subsequently, the combined cross-linking and functionalization of such a polymer was investigated.[71] Several approaches could be performed to reach this goal: in the first route the palladated pincer moieties were reacted with a bis-pyridine, leading to cross-linking *via* the connection of two palladium complexes (Fig. 13a). The second approach utilizes the hydrogen-bonding moiety for cross-linking by the addition of telechelics containing two complementary hydrogen-bonding groups (Fig. 13b). Also a perylene molecule could be utilized for this purpose, introducing a fluorescent dye into the supramolecular polymer. In both cases, the supramolecular binding site not involved in cross-linking was functionalized with monofunctionalized recognition units (not shown in Fig. 13).

Orthogonal supramolecular binding sites can also be exploited for the construction of novel linear systems. Molecules containing a ureidopyrimidinone moiety as well as a terpyridine ligand assemble to linear supramolecular polymers through addition of iron(II) ions (Fig. 14).[72]

In continuing experiments, polymeric spacers were introduced between the two non-covalent binding units. This procedure enhances the solubility of the materials. Investigations of solution and melt viscosity revealed the presence of high-molecular weight species. Moreover, the properties could be tuned by concentration, temperature and the metal ions used.[73]

Metal complexation and host–guest interactions

The introduction of bioactive species into synthetic supramolecular systems could eventually close the gap between natural

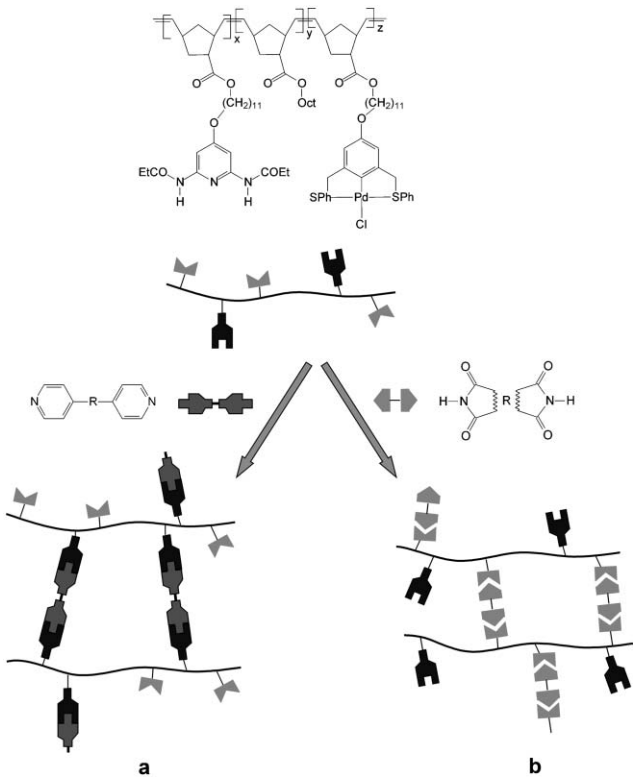


Fig. 13 Schematic representation of cross-linking *via* a palladated pincer (a) and hydrogen-bonding units (b) with bifunctional complementary recognition units.

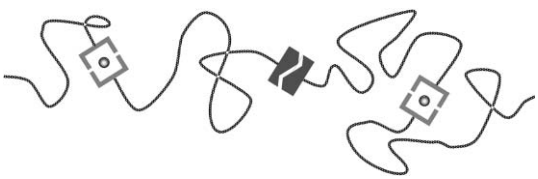
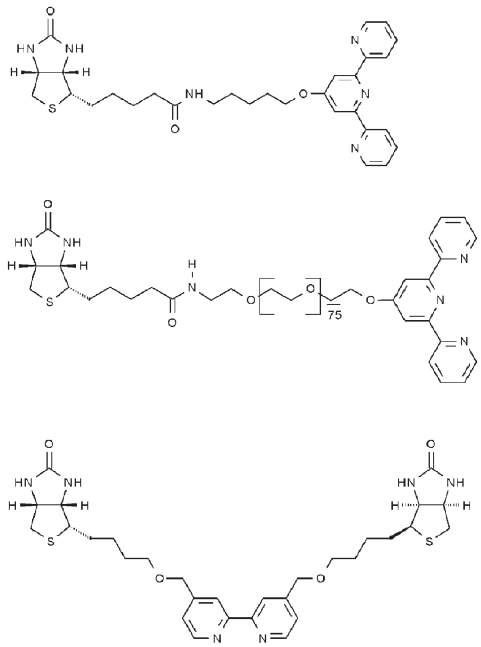


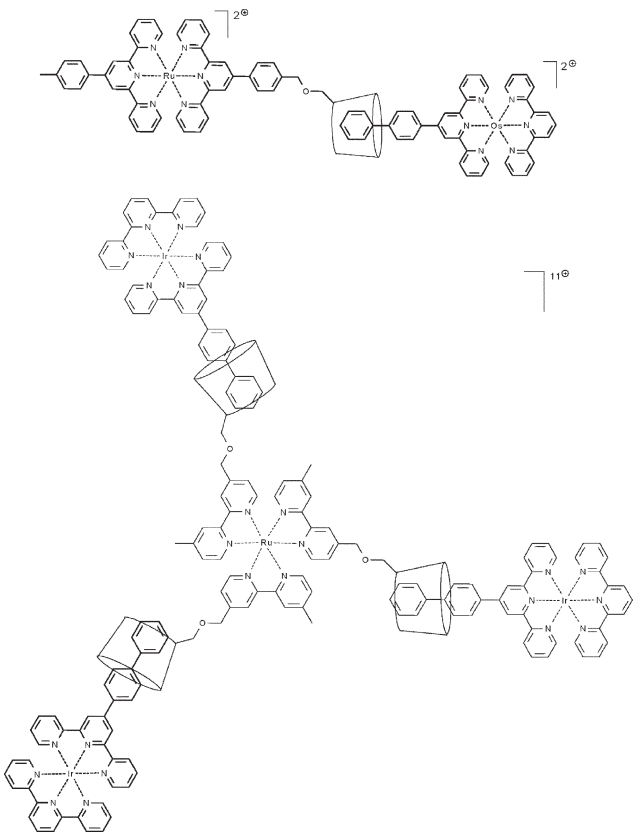
Fig. 14 Schematic representation of a linear polymer composed of alternating hydrogen-bonding units and terpyridine metal complexes.

and synthetic materials. The obtained systems may find potential applications for the construction of biosensors or ''nanoreactors''. Biotin, one of the most prominent natural non-covalent binding units (which forms stable ''complexes'' with the proteins avidin and streptavidin, association constant: 10^{15} mol^{-1}, see above), was recently combined with a terpyridine moiety. The metal terpyridine linker can be tuned regarding stability as well as kinetics and can be reversibly opened by external stimuli. A non-polymeric as well as a polymeric poly(ethylene glycol) linker was used (Scheme 7).[74] Such compounds represent the first link between biochemistry and metallo-supramolecular chemistry and are suitable building blocks for the construction of functional (nano)architectures.

Another recent contribution describes the functionalization of bipyridine with biotin and the subsequent preparation of the corresponding iron(II) complex.[75] This complex is described as a ''redox-biotin bridge'' for potential applications as a biosensor. The addition of avidin to the complex leads to a



Scheme 7 Molecules containing biotin groups and a metal chelator.



Scheme 8 Arrays of terpyridine (bipyridine) complexes and cyclodextrin–guest systems.

change in the Fe(II)/(III) redox signal of cyclic voltammetry, allowing monitoring of the avidin addition. In addition, the three-dimensional orientation of the biotin moieties allows the anchoring of multiple avidin units.

Besides biotin, cyclodextrins were also connected to terpyridine as well as bipyridine ligands. Cyclodextrins are cyclic polysaccharides possessing a cavity that can form strong non-covalent interactions with *e.g.* aromatic compounds. Applying host–guest chemistry, donor–acceptor arrays could be obtained, allowing electron and energy transfer processes (Scheme 8). These systems do not include polymeric architectures up to now, however, polymers could be connected in the future to cyclodextrin-functionalized terpyridine–ruthenium(II) complexes. The cyclodextrin–terpyridine unit could, for example, be modified with linear polymers or introduced into side-chains of terpyridine-containing polymers in a grafting reaction (see above). This methodology would allow the incorporation of the system in polymer matrices for the construction of light-harvesting devices. Such light-harvesting devices within a polymer could represent a step towards plastic solar cells.

Conclusions

Supramolecular chemistry and self-assembly processes have evolved to be one of the most important fields in modern research. Especially polymers containing non-covalent interactions are in the focus, since such supramolecular polymers may find new applications as functional materials. The reversibility of the supramolecular bond could even allow the design and construction of ''smart materials'' with tunable properties. Inspired by nature, where a wide range of supramolecular interactions are used in parallel, this concept was adopted to the field of synthetic polymers. Multifunctionality could be created in a controlled fashion by multiple self-assembly *via* highly-selective ''orthogonal'' supramolecular binding sites. Using this strategy, new multifunctional materials could be constructed, which may find potential applications such as organic LEDs, solar cells or sensors.

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