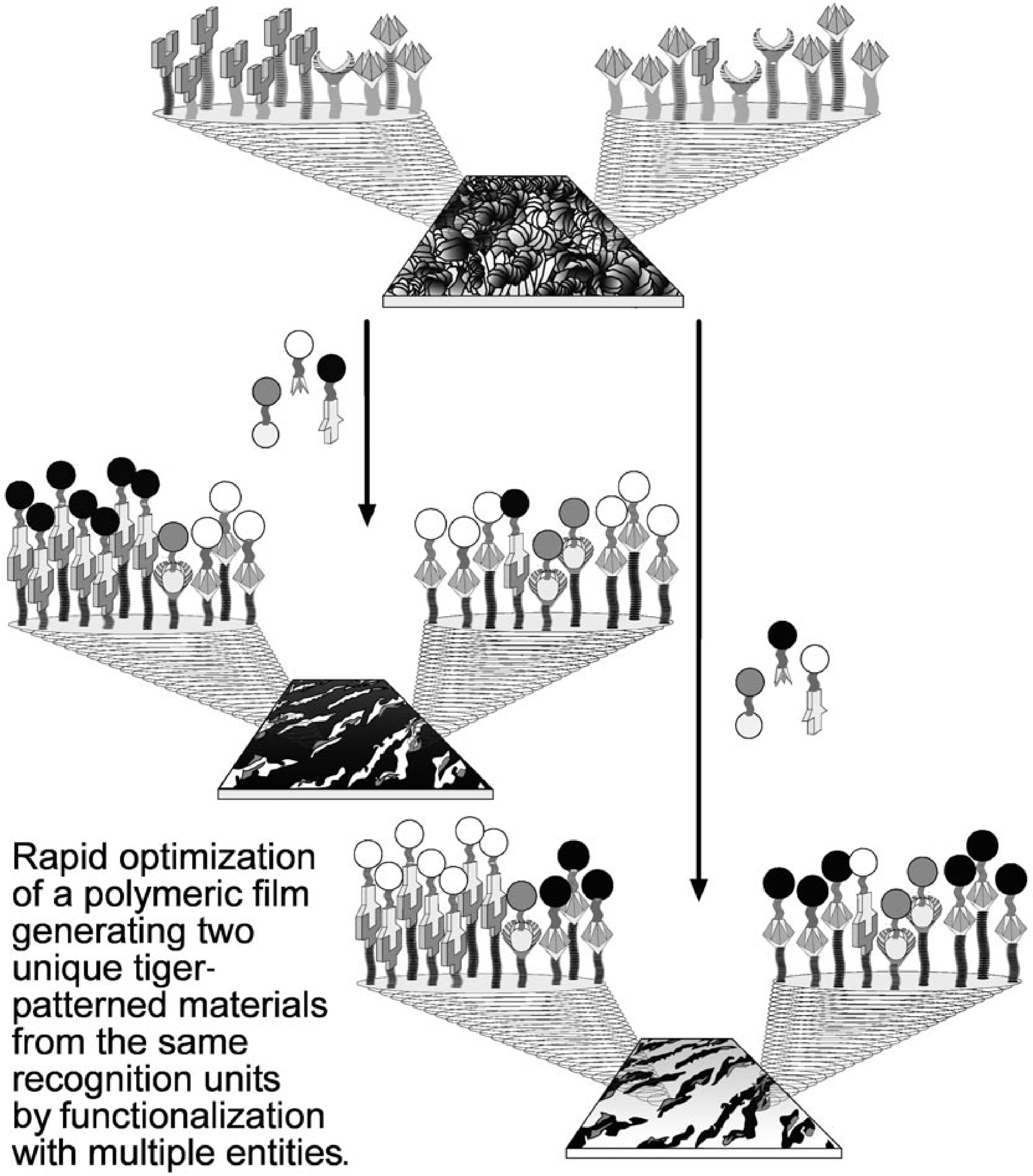

Rapid optimization of a polymeric film generating two unique tiger-patterned materials from the same recognition units by functionalization with multiple entities.

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Multifunctionalization of Synthetic Polymer Systems through Self-Assembly

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Abstract: A straightforward methodology towards the replacement of covalent strategies for the synthesis of multifunctional synthetic materials with a self-assembling strategy that employs multiple noncovalent recognition units to attach multiple functional molecules to a polymeric scaffold is outlined. Design requirements, advantages, and potential applications, as well as the possibility of rapid optimization of materials during the manufacturing process as a result of the parallel character of self-assembly, are presented. While still in its infancy, this novel methodology may overcome several shortcomings of current covalent multifunctionalization strategies and may yield highly complex materials that are extremely difficult or impossible to fabricate with current methods.

Keywords: hydrogen bonds • metal coordination • multifunctionalization • self-assembly • supramolecular chemistry

Introduction

Over the last few centuries, progress in synthetic chemistry has been based on the mastery of the covalent bond. Covalent bond formation was once the only route to create complex molecules with desired functions. Our comprehension and achievements in synthetic chemistry are inextricably dependent on this static covalent foundation, but an upper limit in molecular design using covalent chemistry has been reached at which control, time, and cost all suffer. In the past 40 years there has been an impetus to utilize self-assembly as the practical alternative to covalent-based chemistry in the design and fabrication of complex molecules and functional systems.[1,2] The acceptance of self-assembly as the design strategy for complex and highly functionalized molecules and materials, the focus of this article, is virtually unavoidable if the scientific community continues to use natural systems as an archetype, since all organisms in nature use self-assemble to facilitate a rapid expansion from small covalent units into higher-ordered suprastructures.[3–5] These natural and synthetic systems rely on self-assembling modules, discrete units with a dynamic, specific, and reversible binding that permit the generation of materials and devices at a scale and complexity incomprehensible using covalent methods.[1,4] The fidelity of these self-assembled organic suprastructures is regulated by the complementarity of their recognition units and the final supramolecular assemblies are often multifunctional, that is, able to perform a variety of tasks.

There are recurring recognition motifs found in every biological system that guide the self-assembly of nucleic acids and proteins, the two most prevalent supramolecular biopolymers. These biopolymers form larger supramolecular polymers through the coherence of the recognition motifs that are incorporated into the respective monomers of each covalent biopolymer and yet they are able to perform a myriad of unique tasks in a dynamic physiological environment. Among the most intriguing aspects of self-assembled biomaterials is their multifunctional character; they are able to display, undergo, or catalyze a variety of important functions through molecular recognition using a single self-assembled suprastructure. One example of a multifunctional biomaterial is ATP synthase (Figure 1), a multisubunit transmembrane protein with a molecular mass of 450 kD.[5] This amphiphilic protein is responsible for ATP synthesis. It contains two large functional units that are reminiscent of a merry-go-round, with many smaller subunits all held together by noncovalent interactions. The multiple domains of this supramolecular machine are responsible for 1) anchoring the protein to the cellular membrane; 2) binding an ADP molecule, which allosterically releases a newly synthesized ATP molecule; and 3) translocating protons across the membrane, which facilitates the requisite rotation about its axis enabling this allosterism.[5] All three functions essentially rely on only noncovalent interactions that work in an orthogonal fashion with a nearly perfect fidelity. This is just a cursory examination of this elaborate protein, but it illus-

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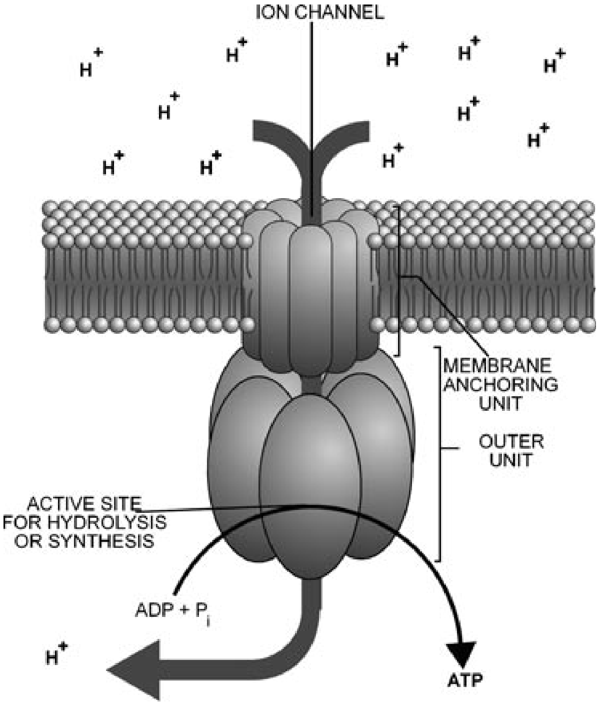

Figure 1. Scheme of the basic functions of the ATP synthase as an example of a multifunctional self-assembled suprastructure; it can be understood as a biomolecular machine.

trates the role of multifunctional domains in a biological system.

In contrast, multifunctionalization in self-assembled synthetic systems is still a nascent field, but it has the potential to create complex materials with a variety of well-defined functions in such important areas as materials science, drug delivery, and biomimetic chemistry.[3,6] In this concept article, we will introduce and expound on the design strategies for multifunctional, self-assembled synthetic materials with an emphasis on polymeric systems using noncovalent interactions. Complex polymeric materials that contain more than one functional group are of utmost importance due to their potential applications in a variety of areas ranging from polymeric light-emitting diodes and photovoltaic cells to drug delivery systems and biosensors. For all these applications, more than one functional group is needed to create a fully functional material. A possible noncovalent strategy towards such materials could be the use of polymeric scaffolds that can be functionalized with small molecules by means of self-assembly. Two routes can be envisioned for the attachment of different functionalities onto such polymeric scaffolds through self-assembly: 1) a statistical mixture of two or more functionalities with a single anchoring recognition unit thereby creating an ill-defined polyfunctional system and 2) a well-defined selective system with two or more functionalities each with a different anchoring recognition unit (Figure 2). While the first strategy may hold promise for a variety of applications, only the second approach allows for full control over the self-assembly process and ultimately the molecule and materials properties. If orthogonality is instilled into the second approach then the manufacturing process is also simplified. This orthogonality would allow for rapid optimization and post-synthetic alterations of multifunctional self-assembled materials. Therefore, in this contribution, we will focus on synthetic systems formed by the second functionalization approach with orthogonality of the recognition units as a prerequisite to multifunctionalization.

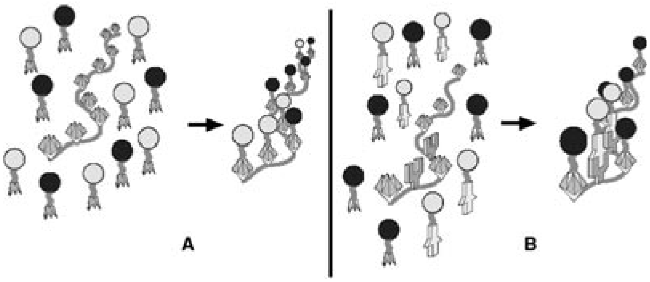

Figure 2. Schematic representation of the multifunctionalization of a polymeric scaffold. A) Ill-defined multifunctionalization by random self-assembly of different small molecules onto a polymeric scaffold by means of a single noncovalent interaction. B) Well-defined multifunctionalization of a polymeric scaffold using several noncovalent interactions in an orthogonal fashion.

Design Requirements of Multifunctional Synthetic Systems

Design considerations for any functional polymeric system are strongly dependent on the application. However, two decisions that must always be made before the creation of any self-assembled polymeric material are the selection of a scaffold amenable to the functionalization and the ideal recognition unit(s).

The chosen scaffold has to be functional group tolerant but still contain reactive groups or molecular recognition units for its subsequent functionalization. Therefore, the scaffold should contain a minimum number of heteroatoms, which will minimize negative interactions between the recognition units and the scaffold during the self-assembly steps, while retaining reactive sites for the fast and quantitative introduction of the molecular recognition units either before or after the formation of the scaffold. A large variety of scaffolds can be envisioned including metal surfaces or nanoparticles, silica-based materials, such as zeolites or fumed silica, dendrimers, or linear polymers. Herein, an emphasis will be put on linear polymeric scaffolds due to their important advantages including a large variety of chemical compositions, established characterization methods, wide synthetic versatility, and ease of processing.

The second design consideration is the choice of the recognition units. The field of self-assembly has yielded a multitude of recognition units to exploit noncovalent interactions.[1–3,7] Requirements for the recognition units to be used in multifunctionalization include fast and quantitative self-assembly steps and the possibility for simple derivatizations and syntheses. A number of weak interactions are imaginable for potential use in self-assembled polymeric materials, but the three main classes that have been reported in the literature are hydrogen bonding, host–guest chemistry, and coordination complexes.[2,7]

A variety of supramolecular hydrogen-bonding polymers have been fabricated with important examples by a number of authors including Meijer, Lehn, Rotello, and Zimmermann (Figure 3),[8–11] while host–guest systems such as calixarenes or ammonium/crown ether interactions have been used to synthesize various supramolecular structures, including threaded complexes and supramolecular polymers (Figure 4).[2,12,13]

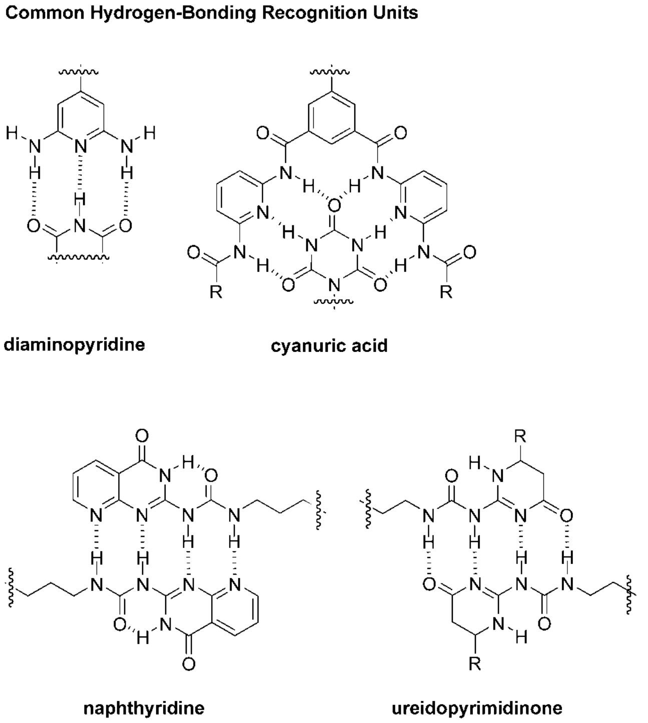

Figure 3. Examples of important hydrogen bonding synthons in the literature.

A large number of metal coordination complexes have been used in the literature to produce self-assembled materials (Figure 5).[7,14] Bipyridine and terpyridine-based metal complexes being two of the most studied supramolecular systems to date, both allow for facile tuning of the interaction strength through the choice of the metal.[2,15–21] Other ligand systems capable of coordinating to metal salts include metallated pincer complexes with phosphine or pyridine ligands and metallated phenanthroline moieties.[22–27] All three classes of recognition events are usually fast and high yielding and the individual recognition motifs are rather simple.

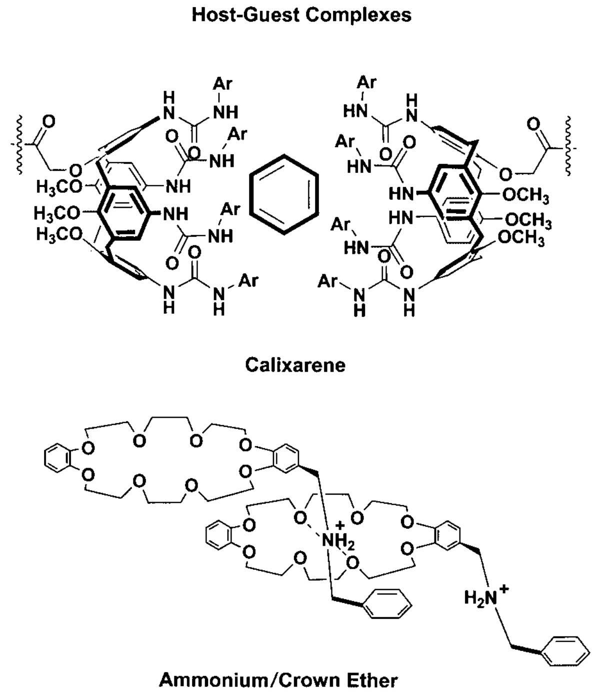

Figure 4. Examples of recognition units used in host–guest chemistry.

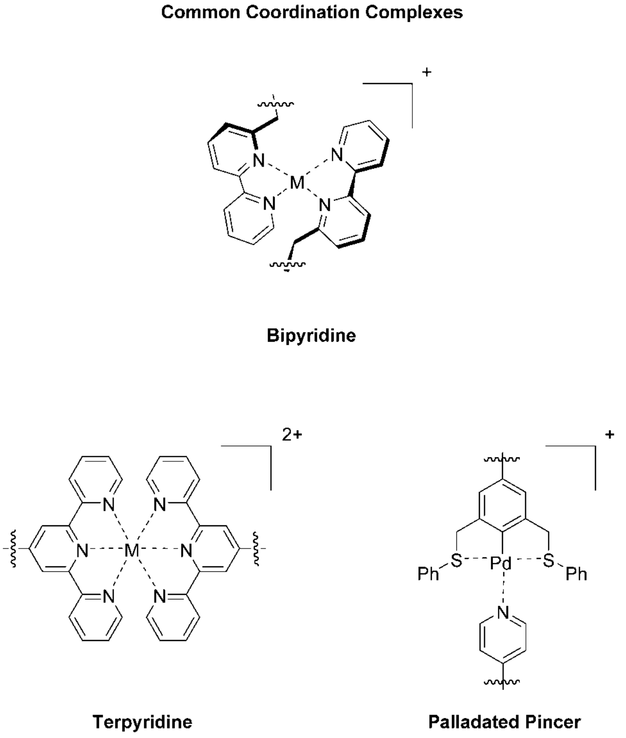

Figure 5. Examples of metal-coordination-based recognition motifs used in supramolecular chemistry.

The key property required for multifunctionalization is that the molecular recognition units chosen do not interfere with each others' self-assembly and that they do not undergo any chemical transformations with each other, the complementary recognition units, or the polymeric scaffold. In summary, all recognition units that are employed in a specific system must be orthogonal to each other. This requirement is consummated by nature's biomaterials. A prime example is the folding of a protein, which can self-assemble an inconceivable number of residues each with functional groups and competitive recognition units.[3] While synthetic chemistry has not reached this level of sophistication, it has started to attract some attention in recent years. For example, in a recent article, Isaacs and co-workers demonstrated

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the orthogonality of a number of hydrogen-bonding units.[28,29] In their study, they showed that different pairs of hydrogen-bonding motifs have a high specificity for each other in the presence of a large number of other hydrogen-bonding donors and acceptors.

Function in Self-Assembly

Function in self-assembly can be viewed as 1) the basic transformation of a molecule through self-assembly, 2) the formation of a complex supramolecular structure through self-assembly, or 3) the formation of a fully functional material for a specific application by means of self-assembly. The first rudimentary classification of function is when the self-assembly step itself imparts function. An example of this functionalization is the formation of acid dimers through self-assembly. The second definition is based on the spontaneous generation of a larger and often more complex structure, that is, a supramolecule. The resulting supramolecular structure often has important macroscopic properties associated with it that are not the mere sum of the properties of its individual parts. On a very basic level, biological molecules such as DNA fall into this category. The third class of self-assembled functionalization can be viewed as the endowment of a specific function or the creation of a material with a well-defined function by using self-assembly. This is epitomized in the structure–activity relationship of proteins and enzymes, which can catalyze post-folding specific reaction sequences that are highly substrate specific.[3–5] These three classifications of function by self-assembly are not exclusive and can often go hand in hand. While nature uses all three strategies, synthetic chemistry is just beginning to introduce multiple functions into supramolecular structures; this point is corroborated by the lack of examples in the literature on the creation of well-defined multifunctional materials through self-assembly.[24]

Most examples in the literature on the synthesis and formation of functional materials through self-assembly rely on a single recognition unit motif. Examples using this strategy include the formation of supramolecular polymers with visco-elastic control, block co-polymers, liquid crystalline systems, hybrid materials, and micellar structures.[2,8,20,21,30,31] Functional self-assembled systems in which external stimuli trigger a molecular shuttle support the idea of synthetic molecular machines and circuitry.[32–35] Furthermore, self-assembled structures have "chaperoned" the generation of larger suprastructures and catalyzed reactions that can be viewed as primitive but promising versions of proteins and enzymes.[36,37]

Multiple Noncovalent Interactions

Self-assembly methodologies that exploit only a single recognition unit will eventually reach their practical limit, and a paradigm shift similar to the displacement of covalent strategies by earlier self-assembled systems will again be required. A logical evolution is multifunctionalization, accomplished through multiple recognition motifs and/or events. Scientists from a variety of disciplines have been inspired by nature's demonstration of multifunctionality in enzymes and proteins, and the quest towards multifunctional self-assembled materials has advanced over the last decade with the successful incorporation of multiple noncovalent interactions and multiple recognition units into new materials enhancing and/or generating function.

Most reports that introduce multiple functions into self-assembled systems by way of several noncovalent interactions have been targeted to understand the relevance of these interactions in nature. To this end, biological systems have been simulated, altered, and dissected in an attempt to determine the influence of multiple noncovalent interactions on their overall stability and to ultimately design and predict biomimetic multifunctional systems. For example, Kool and co-workers illustrated the isosteric removal of hydrogen-bonding sites in nucleosides (Figure 6), demonstrating the influence of π–π stacking on the overall duplex stability of DNA and the DNA replication process.[38] Also, investigations into the design and synthesis of functional peptidal systems have shown the importance that a variety of noncovalent aromatic interactions have on protein folding in these small peptide models.[39,40] In this example, the peptide sequences also contained a number of other noncovalent interactions, such as hydrogen bonding and coulombic interactions, creating a multifunctional scaffold.

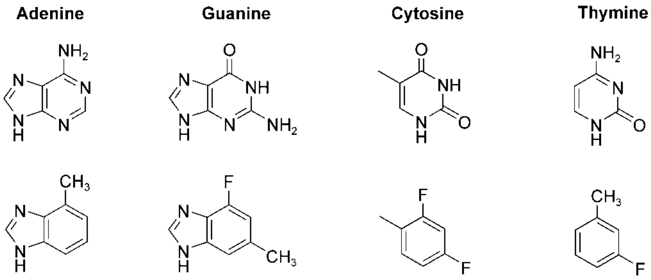

Figure 6. Nucleic acid bases and their isosteric analogues.

There are only a few examples in the literature of multiple noncovalent interactions used in purely synthetic systems that can either lead to enhanced binding of guest molecules at a single site, or which can be segregated into distinct multiple recognition units. The first classification can be understood as a multi- or polyvalent stabilization of a guest molecule and has been used in dendritic and polymeric systems.[2,41] In one interesting example, different recognition units bound to a surface can increase the association of an analyte through multivalent interactions, creating synthetic receptors with possible applications in sensing technologies (Figure 7).[42]

The last case of multiple noncovalent interactions, those used as different recognition units within a discrete assembly was first realized in 1997 by Reinhoudt and co-workers.[43] They combined pincer metal complexes and hydrogen-bonding units to form metallodendrimers. This report clearly showed for the first time that a well-defined material can be synthesized by the sequential use of two independent nonco-

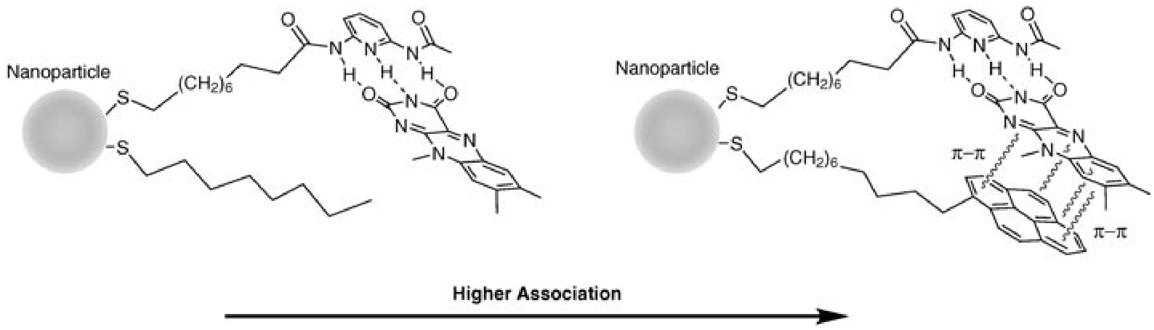

Figure 7. The use of multiple weak interactions to enhance the binding of a guest molecule.

valent interactions, thereby establishing a new methodology outlining the potential such a strategy might hold for materials science (Figure 8).

More recently, Schubert and co-workers functionalized the termini of small molecules with hydrogen bonding and terpyridine metal coordination units.[41] Self-assembly of these small molecules by using hydrogen bonding and metal coordination led to the formation of A–B copolymers.[44] These two examples display the principle of orthogonality within multiple interactions, a prerequisite for multifunctionalization in current and future systems. In both examples, the self-assembly steps act as adhesive agents, facilitating dendrimer or polymer formation, but they do not impart multifunctionality to the materials.

Multifunctionalization

Currently there are only two systems reported in the literature that have the characteristics of multifunctional polymeric systems. The first is based on poly(vinyl pyridine) and has been reported by the group of Ikkala (Figure 9).[42] Here

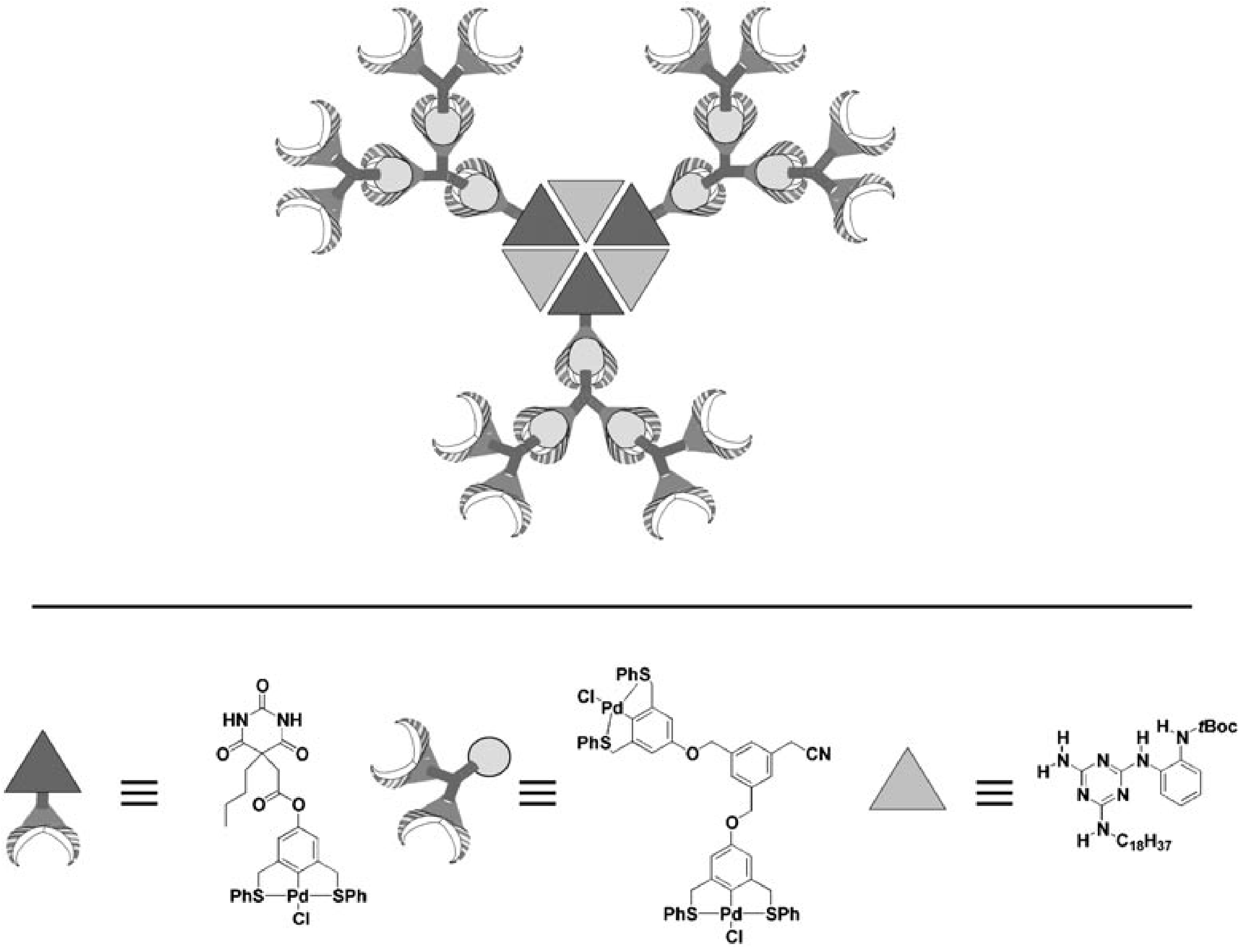

Figure 8. Synthesis of metallodendrimers through the step-wise use of metal coordination and hydrogen bonding.

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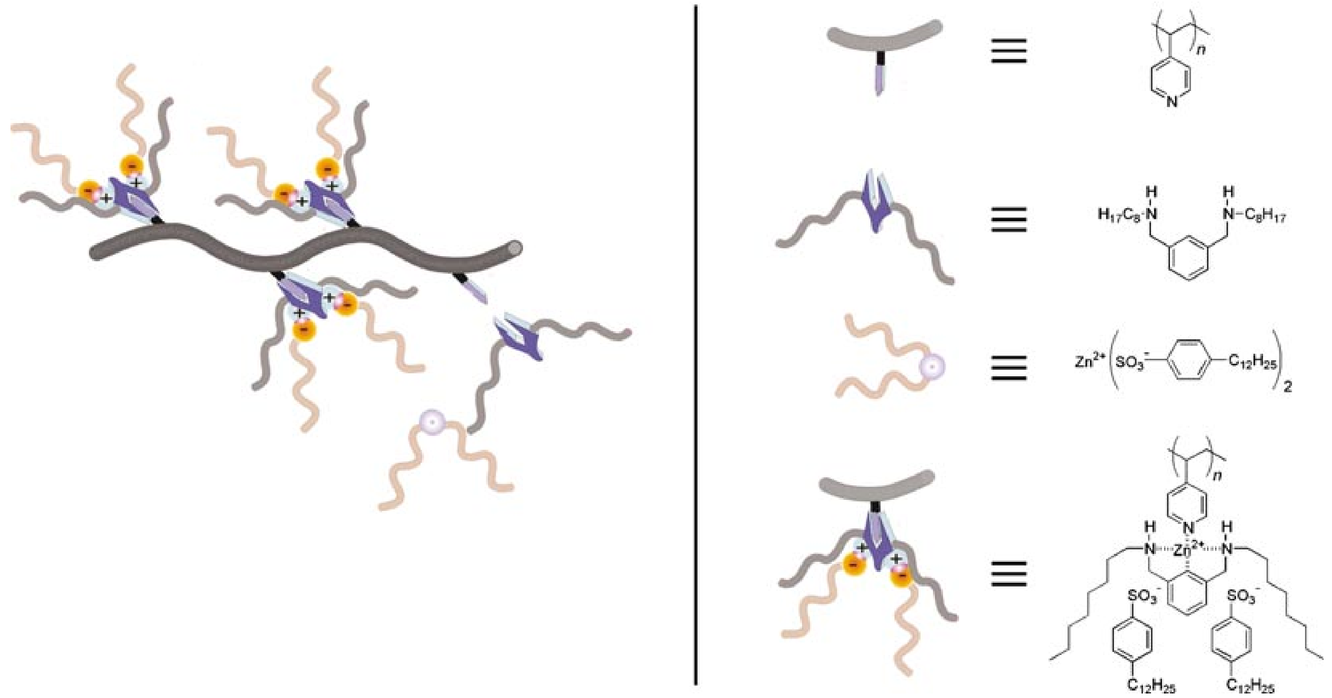

Figure 9. Synthesis of a multifunctional poly(vinylpyridine) functionalized with two alkyl chains.

the pyridine moieties at each repeat unit can coordinate to metal ions with pendant functionalities resulting in the formation of a functional, charged metal complex. This ionic species can then be further functionalized through the selection of the counter ion.[45] While Ikkala and co-workers do not report on the introduction of several functional groups using this strategy, the system has the potential for multifunctionalization by using two different functional groups for the coordination step and the counterions, and the initial design strategy of coordinating two different alkyl chains serves as a proof-of-principle for this unique system.

The second system has been reported by our group and goes by the name "universal polymer backbone" (UPB).[24,46] It is a materials design strategy that has been maturing in our lab for the last four years and was conceptually illustrated in a review by Lehn in 2002.[30] The design is based on a polymeric scaffold that contains a number of different recognition motifs. By using multiple self-assembly strategies, the polymeric scaffold can be functionalized with a wide variety of side chains or functional groups (Figure 10), bestowing several advantages to the system.

First, the processability of a polymeric material makes it a candidate for use in everyday applications. Second, introduction of a large number of functional groups can be fast and quantitative. Third, the same polymeric scaffold can be used for a wide variety of materials suggesting the name "universal polymer backbone". Fourth, the multifunctionalization can be a quick and simple one-pot step, due to the parallel nature of each self-assembly event. These advantages in the ideal UPB design would allow for rapid optimization and streamlining of the manufacturing processes by eliminating the inherent multiple steps required in the production of any covalent material. Therefore, this methodology may open up new avenues in materials design, which may not be accessible or practical by a covalent methodology.

What separates this methodology from the majority of self-assembly strategies in polymer chemistry outlined above is the use of multiple noncovalent interactions. Its distinction from those that have already used multiple interactions

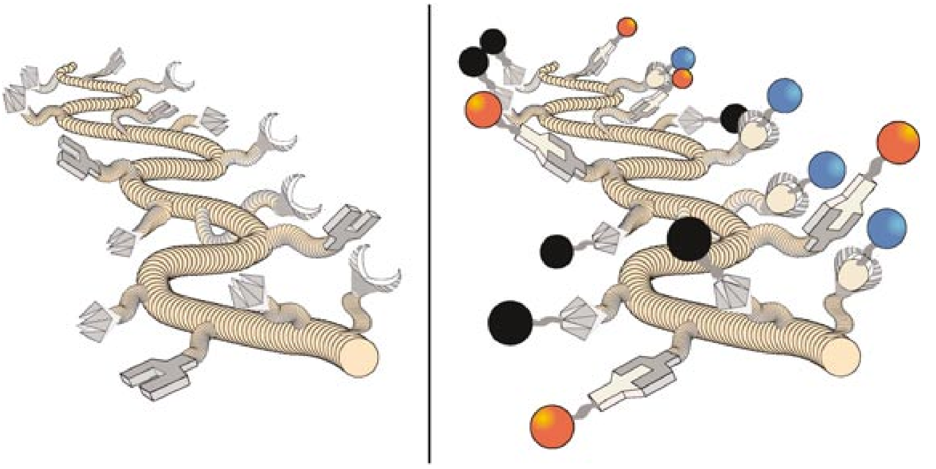

Figure 10. Multifunctionalization of a polymer at three recognition sites: hydrogen bonding (red), metal coordination (blue), Coulombic interaction (black).

is that in all other cases the goal is not the introduction of multifunctionality, but appears to be the establishment of orthogonality, since the final structure could have been realized through a single interaction. The UPB uses orthogonality as a requisite design guideline, permitting simultaneous multiple interactions, the interactions themselves taking a subordinate role to their tethered functionality.

Returning back to the fundamental design requirements for a multifunctional self-assembled system, we first had to select the polymeric scaffold. We decided to use a poly(norbornene)-based polymer backbone that has a variety of important properties and advantages. First, norbornenes can be polymerized by means of ring-opening metathesis polymerization (ROMP), a polymerization method that is often living and fully functional-group tolerant when employing Grubbs' ruthenium initiators.[47] Second, ROMP-based polymers have been used extensively for a variety of applications, including high impact corrosion resistant materials, such as piping and ballistics containment, marine antifouling agents, sports equipment, along with dental and pharmaceutical products, and these polymers have found their way into a number of industrial applications.[48] The identification of the ideal recognition units was the second step in the design of the UPB. We have exploited hydrogen-bonding- and metal-coordination-based recognition units in our laboratory. The hydrogen-bonding recognition units are based on either diaminopyridines or cyanuric acids.[24,43,46] Furthermore, a variety of metal-coordinating recognition units were employed, including metallated pincer complexes and bipyridine-based compounds.[24–27] It is important to note that Grubbs' ruthenium initiators are fully tolerant of any ancillary functional group or metal complex, and we have demonstrated the living character of the ROMP of most monomers as well as determined the polymerization kinetics, thereby giving us full control over the polymerization and allowing for the designed synthesis of random or block copolymer structures.[25]

While the self-assembly methodology for each individual recognition motif has been reported in the literature,[2,25,27,49] none of these studies investigated the orthogonality of these recognition motifs, a prerequisite for their use in multifunctional materials. The orthogonality of random copolymers containing 2,6-diaminopyridine and palladated pincer complexes was recently unequivocally proven by us using a variety of techniques, including NMR spectroscopy, differential scanning calorimetry, and titration experiments.[24] We have shown that the self-assembly process can proceed through three possible pathways (Figure 11). The first pathway (**A**) selectively functionalizes all hydrogen-bonding recognition units with thymine. The pincer units, unaffected during the hydrogen-bonding step, are then quantitatively functionalized with a pyridine moiety. The alternate self-assembly process (**B**), starting with metal coordination followed by hydrogen bonding, was also successful. Of particular importance is the third option (**C**), in which all the receptors and substrates are thrown into the mix and each unit finds its complementary counterpart without any noticeable interference. This is in accordance with the recently reported self-

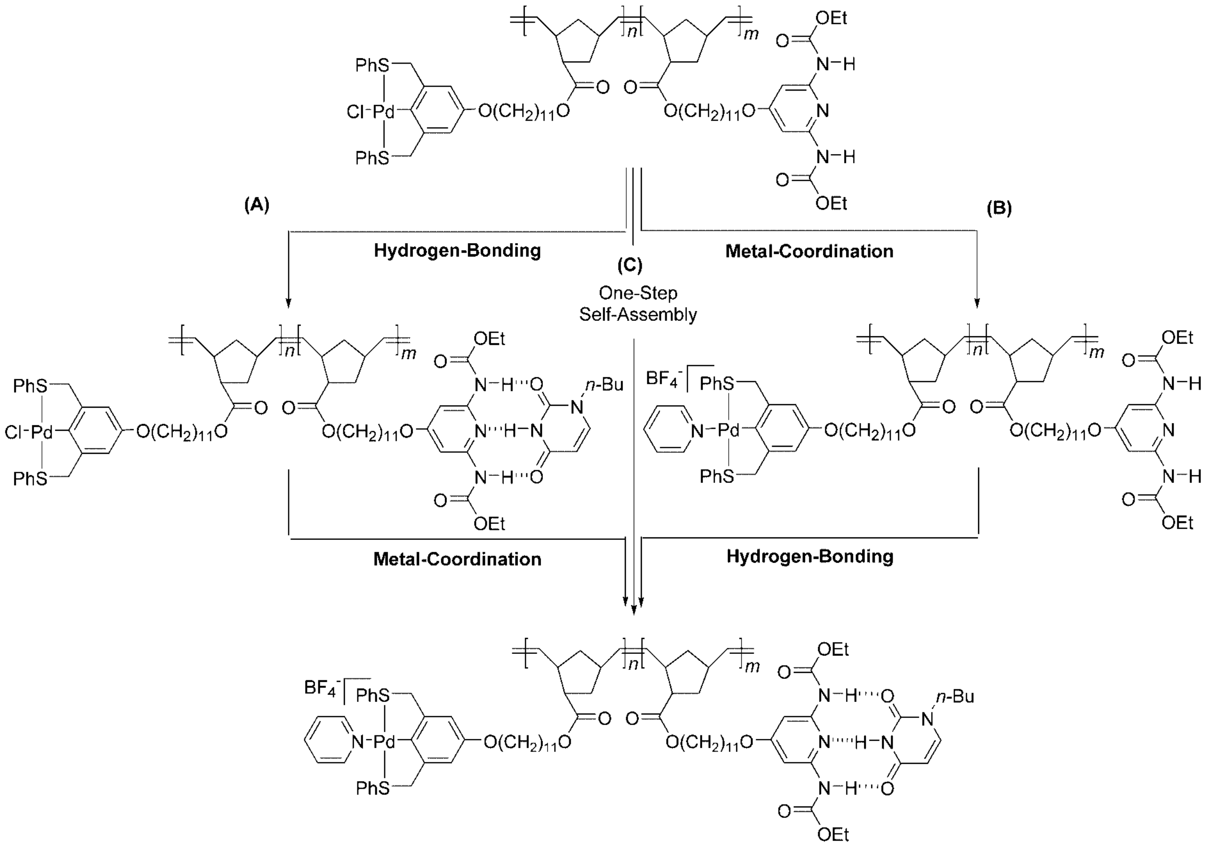

Figure 11. Three pathways to the multifunctionalization of the UPB.

sorting of hydrogen-bonding recognition units,[28,29] and clearly demonstrates that the UPB scaffold can be functionalized in one simple step to afford rapidly optimized multifunctional materials.[24] It is important to note that the properties of the final polymeric material are independent of the strategy used, giving us unprecedented control over the materials functionalization step.

Physical gels have previously been prepared using well-defined noncovalent interactions,[22,50,51] but we recently communicated the first example of multifunctional materials by combining noncovalent cross-linking with noncovalent polymer functionalization using the UPB strategy.[52] Terpolymers containing an alkyl spacer, a pincer complex, and either 2,6-diaminopyridine or cyanuric acid have been synthesized. A perylene unit, which in itself is bestowed with a number of important functions and has been used in the design and synthesis of a variety of electro-optical materials,[53] is used as a noncovalent crosslinker for the UPB. The 2,6-diaminopyridine recognition units along the UPB act as receptors for the perylene (**1**), while the palladated pincer complexes on the UPB remain free for further functionalization using either nitrile (**2**), pyridine (**3**), or phosphine (**4**) containing molecules (Figure 12).

A crosslinked material can also be generated by reversing the cross-linking/functionalization sequence and recognition units used by coordinating bisfunctionalized pyridine ligands onto the palladated pincer complexes, leaving all hydrogen bonding sites open for further UPB functionalization. These examples clearly demonstrate the potential of the UPB in materials design and synthesis. It can be envisioned that more complex methodologies might be developed through the introduction of a third recognition motif, bringing this synthetic multifunctionalization strategy closer and closer to its ideal model in nature, the protein.

Conclusion

Over the last decade, the importance of self-assembly as a synthetic tool in the fabrication of polymeric materials has increased dramatically due to the complex chemical nature of current materials. Furthermore, current research efforts in polymer science are targeted towards the rational design of even more complex materials that are often based on a larger number of functions or contain several well-defined functional substructures; that is, they are multifunctional. It is evident that covalent chemistry cannot be the synthetic strategy of choice for these materials. Nature clearly outlines the use of multiple noncovalent interactions as the design strategy towards the synthesis of its multifunctional biomaterials. In the last five years, a very limited number of synthetic polymeric systems that have either been fabricated through simulating nature's self-assembly methodologies or have been suggested have begun to emerge in the literature. In this concept article, we reviewed the current progress of the field and suggested basic important design aspects. By reviewing the literature, it becomes clear that the field of multifunctional synthetic polymeric systems has a bright future. All fundamental self-assembly studies towards the creation of self-assembled multifunctional materials have been carried out. Furthermore, polymerization strategies are available that allow for the controlled incorporation of func-

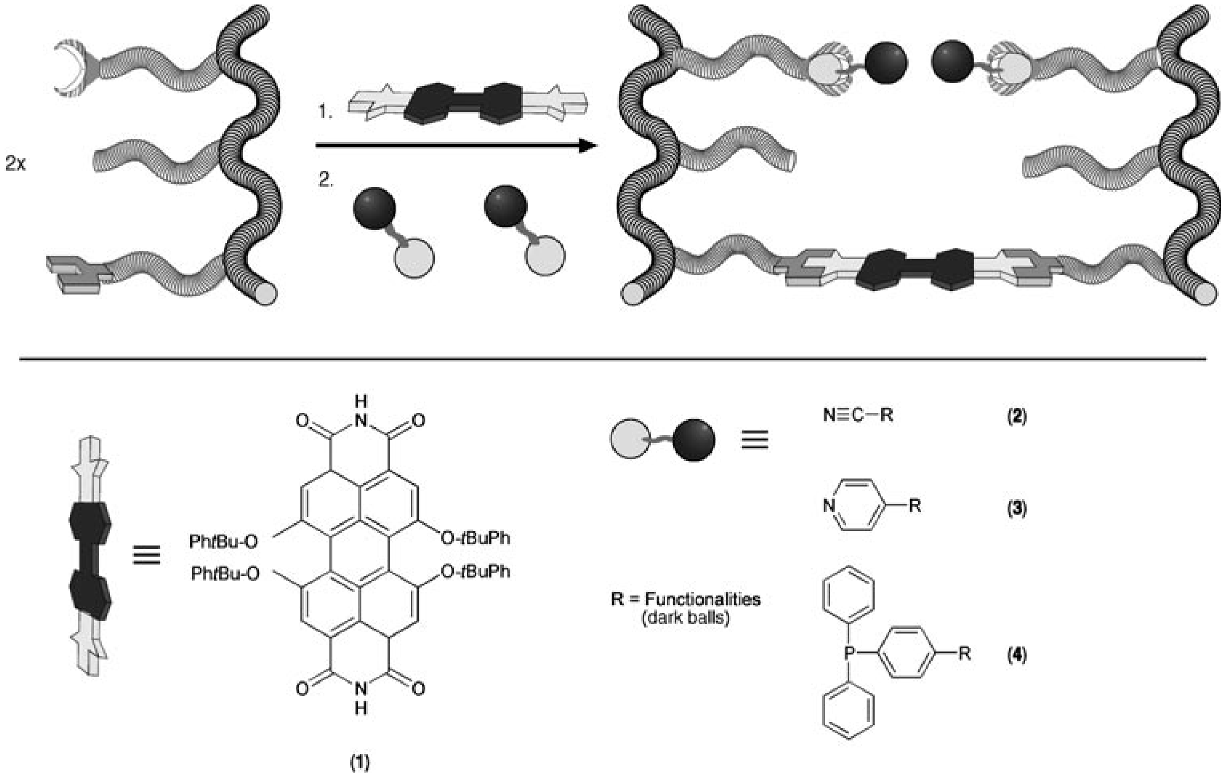

Figure 12. Schematic representation of the cross-linking/functionalization strategy of the UPB.

tional monomers into homo, random, or block copolymers. So what is missing to take this field to the next level? Clearly the self-assembly methodologies towards the creation of multifunctional materials are currently limited. Only two strategies are reported in the literature that describe the use of multiple and orthogonal noncovalent interactions in the synthesis of multifunctional materials, while nature uses a multitude of methodologies towards such a goal. These limited methodologies clearly hamper the expansion of the field. However, with the recent interest in multifunctional polymeric systems and the clear advantages of self-assembly more strategies are expected to be developed in the foreseen future.

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