Engineering Orthogonality in Supramolecular Polymers: From Simple Scaffolds to Complex Materials

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CONSPECTUS: Owing to the mastery exhibited by Nature in integrating both covalent and noncovalent interactions in a highly efficient manner, the quest to construct polymeric systems that rival not only the precision and fidelity but also the structure of natural systems has remained a daunting challenge. Supramolecular chemists have long endeavored to control the interplay between covalent and noncovalent bond formation, so as to examine and fully comprehend how function is predicated on self-assembly. The ability to reliably control polymer self-assembly is essential to generate "smart" materials and has the potential to tailor polymer properties (i.e., viscosity, electronic properties) through fine-tuning the noncovalent interactions that comprise the polymer architecture. In this context, supramolecular polymers have a distinct advantage over fully covalent systems in that they are dynamically modular, since noncovalent recognition motifs can be engineered to either impart a desired functionality within the overall architecture or provide a designed bias for the self-assembly process.

In this Account, we describe engineering principles being developed and pursued by our group that exploit the orthogonal nature of noncovalent interactions, such as hydrogen bonding, metal coordination, and Coulombic interactions, to direct the self-assembly of functionalized macromolecules, resulting in the formation of supramolecular polymers. To begin, we describe our efforts to fabricate a modular poly(norbornene)-based scaffold via ring-opening metathesis polymerization (ROMP), wherein pendant molecular recognition elements based upon nucleobase-mimicking elements (e.g., thymine, diaminotriazine) or SCS-Pd[II] pincer were integrated within covalent monofunctional or symmetrically functionalized polymers. The simple polymer backbones exhibited reliable self-assembly with complementary polymers or small molecules. Within these systems, we applied successful protecting group strategies and template polymerizations to enhance the control afforded by ROMP. Main-chain-functionalized alternating block polymers based upon SCS-Pd[II] pincer−pyridine motifs were achieved through the combined exploitation of bimetallic initiators and supramolecularly functionalized terminators. Our initial design principles led to the successful fabrication of both main-chain- and side-chain-functionalized poly(norbornenes) via ROMP.

Utilizing all of these techniques in concert led to engineering orthogonality while achieving complexity through the installation of multiple supramolecular motifs within the side chain, main chain, or both in our polymer systems. The exploitation and modification of design principles based upon functional ROMP initiators and terminators has resulted in the first synthesis of main-chain heterotelechelic polymers that self-assemble into A/B/C supramolecular triblock polymers composed of orthogonal cyanuric acid−Hamilton wedge and SCS-Pd[II] pincer−pyridine motifs. Furthermore, supramolecular A/B/A triblock copolymers were realized through the amalgamation of functionalized monomers, ROMP initiators, and terminators. To date, this ROMP-fabricated system represents the only known method to afford polymer main chains and side chains studded with orthogonal motifs. We end by discussing the impetus to attain functional materials via orthogonal self-assembly. Collectively, our studies suggest that combining covalent and noncovalent bonds in a well-defined and precise manner is an essential design element to achieve complex architectures. The results discussed in this Account illustrate the finesse associated with engineering orthogonal interactions within supramolecular systems and are considered essential steps toward developing complex biomimetic materials with high precision and fidelity.
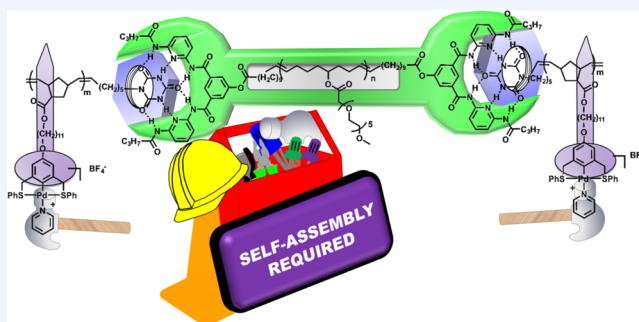
INTRODUCTION

Since the inception of supramolecular chemistry in the 1970s,[1] the field has developed into an architectural science wherein the interplay of covalent and noncovalent bonds can be manipulated to achieve well-defined molecular[2] and macromolecular targets[3] that have the potential to echo the simplicity and efficiency of Nature. Nature juxtaposes molecular building blocks in a precise manner to generate functional scaffolds that rely upon multiple mutually orthogonal interactions to sustain complex assemblies. The prospect of bridging the gap between synthetic and natural systems continues to motivate chemists to adapt analogous design principles that afford materials ranging from novel catalysts[4] to drug delivery vehicles.[5] A major
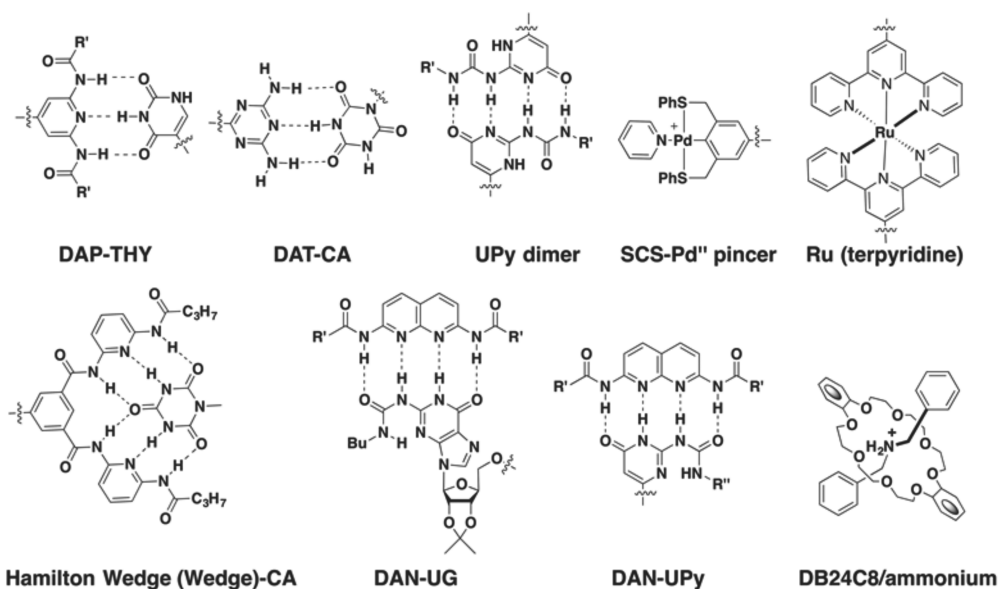
Figure 1. Commonly exploited supramolecular motifs.

impediment to mastering complexity[6] lies in achieving the fidelity and simplicity of Nature's constructs, particularly as it relates to engineering multiple precise and orthogonal interactions into one cohesive unit. The concept of orthogonality[7] has revolutionized several areas of covalent chemistry, initially being coined in the context of chemoselectivity and protecting groups and since expanding to include simultaneous transformation reactions.[7] More recently, orthogonality has emerged in conjunction with noncovalent chemistry,[8] denoting the simultaneous engineering of mutually compatible (i.e., noninterfering) supramolecular interactions within a fidelitous framework.[7] Indeed, synthetic efforts to rival the complexity of biological systems are dependent upon achieving a panoply of orthogonal noncovalent interactions within a desired architecture.

We developed a methodology that utilizes multiple non-covalent interactions, in a general and precise way, to achieve functional supramolecular systems with a high dimension of orthogonality. Side-chain supramolecular copolymers and terpolymers[9] functionalized with a variety of mutually compatible molecular recognition units can be fabricated using ring-opening metathesis polymerization (ROMP).[10] The side-chain-functionalized polymers not only demonstrate orthogonal self-assembly[11] with complementary units but can exhibit tunable mechanical properties in the presence of monotopic and ditopic complementary molecules.[12] In addition, supramolecular polymers containing both main-chain and side-chain functionalization were achieved.[13] Furthermore, heterotelechelic polymers exhibited an orthogonal self-assembly en route to the first ABC supramolecular polymer system.[14] From a synthetic standpoint, the high tolerance of ROMP to supramolecular motifs provided access to the target functionalized polymer systems with relative ease. From a supramolecular standpoint, the key to achieving more complex yet precise assemblies lies in exploiting the orthogonality of specific noncovalent interactions.

SUPRAMOLECULAR INTERACTIONS

Cohesive noncovalent interactions involve highly directional forces including coordination bonds (100−300 kJ mol^{-1}),

hydrogen bonds (4−120 kJ mol^{-1}), $\pi\cdots\pi$ stacking (2−50 kJ mol^{-1}), and ion$\cdots\pi$ interactions (5−80 kJ mol^{-1}).[15] Other forces such as ion−ion and van der Waals interactions are also prominent but from an engineering perspective offer less utility toward the rational design of materials, because they are less directional. Historically, hydrogen bonding has been the most exploited in this context, largely owing to the wealth of such noncovalent interactions in biosystems.[16] Accordingly, the engineering of hydrogen-bonding motifs within supramolecular polymers is aided by exploitation of the high directionality manifested by nucleobases (e.g., thymine (THY), uracil, guanosine).[17]

Seminal work utilizing the complementary recognition of ditopic uracil and diaminopyridine (DAP) monomers to achieve main-chain supramolecular polymers was reported by Jean-Marie Lehn,[18] wherein the main chain was sustained by three-point interactions. Similar three-point hydrogen bonds have also been achieved using DAP with THY or a diaminotriazine (DAT) framework with cyanuric acid (CA).[19] These interactions (Figure 1) are all based upon a DAD−ADA arrangement of hydrogen-bond donors (D) and hydrogen-bond acceptors (A) within the assembly and exhibit K_a values of 10^2−10^3 M^{-1} in CDCl$_3$.[20]

In 1988, Andrew Hamilton designed a supramolecular receptor based upon N^1,N^3-bis(6-butyramidopyridin-2-yl)-5-hydroxyisophthalamide, colloquially referred to as the Hamilton wedge (Wedge).[21] The Wedge contains six inwardly positioned hydrogen bonds in a DADDAD arrangement, and can self-assemble with CA and other barbiturates ($K_a = 10^4$−10^5 M^{-1} in CDCl$_3$).[19] By the 1990s, self-complementary motifs based upon 2-ureido-4[1H]-pyrimidinone (UPy) emerged as desirable building blocks, owing to the ability to sustain four highly directional hydrogen bonds while exhibiting $K_{dim} > 10^5$ M^{-1} in CDCl$_3$.[22] Integrating UPy motifs within main-chain supramolecular polymers has been accomplished by Meijer,[23] Sijbesma,[24] and Schubert.[25] Other prominent hydrogen-bonding pairs include 2,7-diamido-1,8-naphthyridine (DAN)−ureidoguanosine (UG)[26] and UPy−DAN (Figure 1).[27]

Supramolecular interactions founded upon metal coordination and Coulombic interactions (Figure 1) have also been
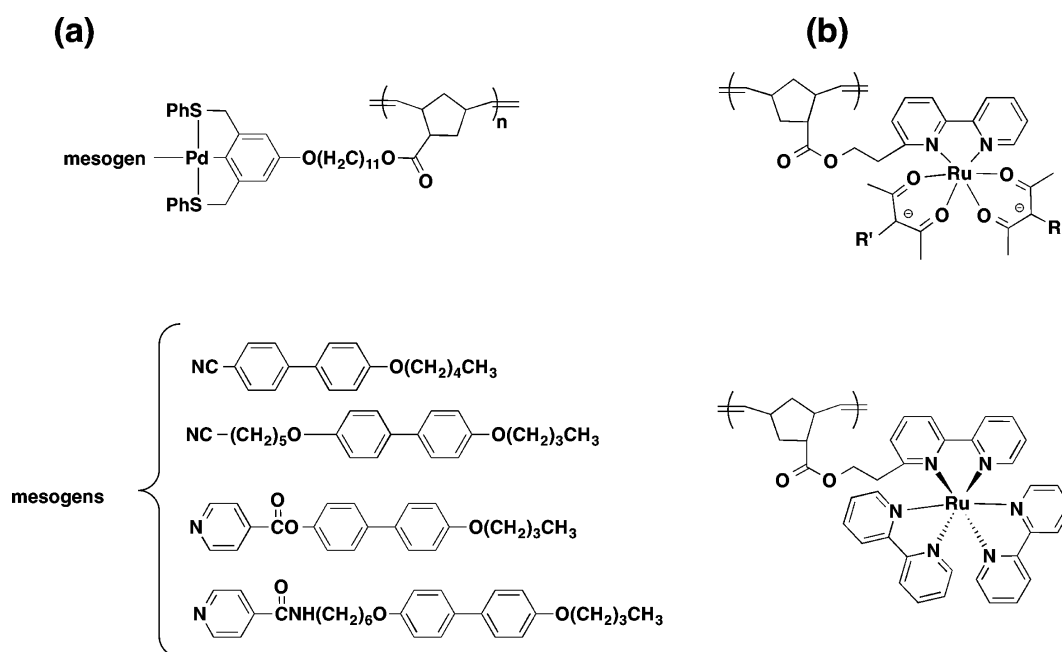
Figure 2. ML_x side-chain-functionalized supramolecular polymers.

exploited, owing to their highly directional nature.[15] Efforts toward the production of functional metallosupramolecular polymers have resulted in the utilization of pyridine-based functionalities (e.g., terpyridine,[28] bipyridine[29]) containing molecular recognition-capable coordination spheres that engage in high fidelity self-assembly with metals ($K_a > 10^9$ M^{-1} in DMSO/H_2O).[28] More recently, the self-assembly of dibenzylammonium cations with dibenzo[24]crown-8-ethers (DB24C8) has emerged to engineer pseudorotaxane-containing supramolecular polymers, with K_a values on the order of 10^4 M^{-1} in CDCl$_3$.[30] Additional polymer systems featuring cucurbiturils that exploit host−guest interactions have been reported by Scherman.[31]

Given the wealth of highly directional noncovalent interactions, it is perhaps not surprising that supramolecular polymers are highly tunable scaffolds, wherein a degree of flexibility that is absent in covalent systems can be abused to engineer target architectures. Each prominent supramolecular interaction exhibits a reversible nature, with the strength of each interaction alterable using external stimuli (e.g., temperature, solvent).[32] In addition, other variables, such as topicity and arrangement of donors and acceptors within a hydrogen-bonding synthon, can be exploited to favor self-assembly to higher ordered structures.[33] The successful pursuit to rival natural complexity lies in the ability to fully comprehend all of the facets that influence molecular recognition and self-assembly, while exploiting their modular nature to engineer systems with a high density of orthogonality.[7]

■ DESIGN PRINCIPLES

Our initial exploits led us to determine whether polymeric scaffolds functionalized with recognition units could be prepared in a modular and controlled manner. To attain well-defined polymers, we turned to take advantage of the functional group tolerance and living nature intrinsic to ROMP.[35] Although monomer choice is limited, the versatility and ability to precisely position functionalities makes ROMP appropriate to produce a library of complex supramolecular polymers.

Whereas other polymerization methods such as ring-opening polymerization (ROP),[26b] atom transfer radical polymerization (ATRP),[36] and reversible addition-fragmentation chain transfer (RAFT)[34] have emerged as fully capable of fabricating supramolecular polymers, ROMP is able to afford side-chain- and main-chain-functionalized polymers in a well-defined and precise manner.[37] Having established ROMP as our synthetic *modus operandi*, we set out to design a universal polymer backbone (UPB)[35] composed of supramolecularly relevant functionalities and capable of self-assembly in the presence of small molecules to afford a library of densely functionalized polymeric materials. To achieve our UPB design, several prerequisites had to be satisfied: the self-assembly had to be highly directional in the presence of complementary moieties and eventually allow for a variety of orthogonal recognition units to be installed along the polymer backbone, leading to a tunable platform.

Our interests in engineering a UPB stemmed from the desire to introduce functionality within the side chains or along the main chain of a polymer scaffold, leading to robust materials.[38] Side-chain functionalization[9] has been mainly utilized by Rotello,[39] Sleiman,[40] Tew,[28,41] Fréchet,[42] Kato,[43] and Zimmerman,[44] affording materials such as liquid crystals,[43] owing to an inherently modular synthesis. The majority of side-chain-functionalized systems feature a covalent block studded with pendant recognition motifs, with the most common scaffolds based upon poly(acrylates),[9,44] poly(styrenes),[25,42] poly(siloxanes),[43] and poly(norbornenes).[9,37] Whereas side-chain systems are invariably based upon polymer blocks, main-chain systems[45] can comprise either discrete functional molecules that noncovalently interact to form a polymeric system or end-functionalized polymers that effectively act as macromonomers.[26b] Although the former approach is most common, systems based on poly(peptides),[46] poly(ethylene),[47] and poly(caprolactone)[25,35,45] have been utilized by a number of groups including Meijer,[46] Rowan,[47] Fraser,[35] and Schubert[25] affording supramolecular materials that exhibit optically
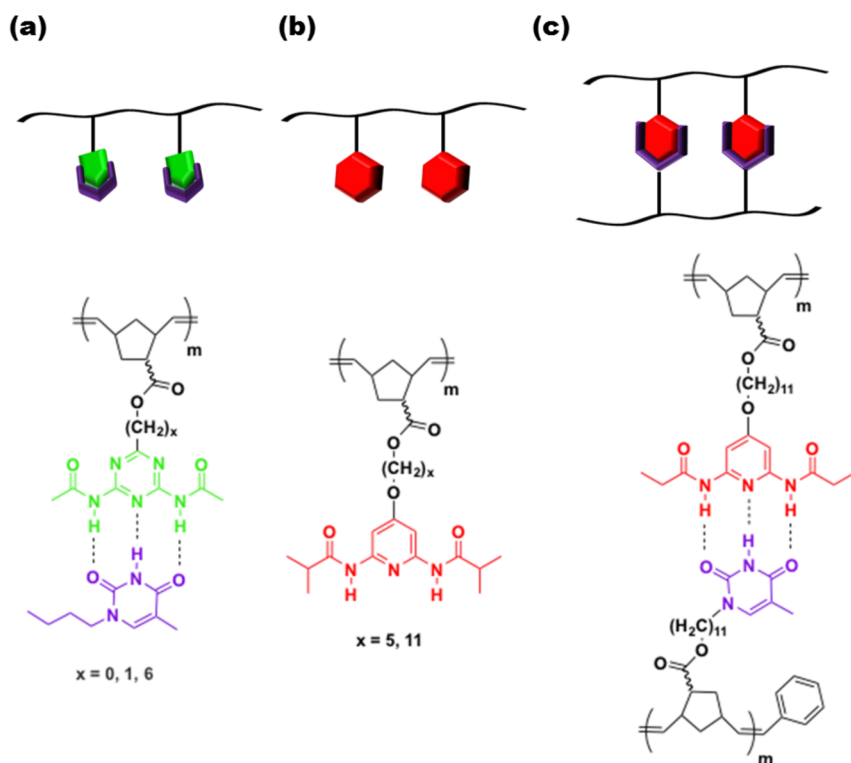
Figure 3. (a) Protecting group strategy, (b) DAP-functionalized poly(norbornene), and (c) template polymerization.

healable[47] and stimuli-responsive[25] behaviors, as well as potential tissue engineering scaffolds.[46]

Our first steps toward the design of an easily tunable polymer backbone utilized the ROMP of substituted norbornenes that offered metal coordination as a means to self-assembly.[35,48] Specifically, a norbornene side-chain functionalized with a palladated sulfur−carbon−sulfur (SCS) pincer ligand was investigated,[35] owing to the quantitative nature associated with the coordination step and the wealth of suitable ligands to tether to the polymer scaffold (Figure 2a). Self-assembly in the presence of either nitrile- or pyridine-based ligands resulted in quantitative coordination, revealing the ability of the polymer backbone to act as a platform to afford a variety of materials.[35] Efforts to incorporate other metal coordination-based motifs resulted in a 2,2′-bipyridine (2,2′-bpy)-functionalized norbornene. Subsequent self-assembly with ruthenium or palladium, and 2,4-pentanedione or 2,2′-bpy, followed by ROMP, afforded poly(norbornene)s studded with pendant Ru(2,2′-bpy)$_3$, Pd-(2,2′-bpy)$_2$, or heteroleptic Ru complexes (Figure 2b).[48] Related studies by Schubert and Sleiman have also utilized ROMP to fabricate ML$_x$-containing supramolecular polymers that exhibit properties intrinsic to the metal complex (e.g., luminescence, fluorescence).[25,40] Additional ML$_x$ containing polymers have been reported by Tew,[28,41] Rowan,[47] and others.[49]

To increase the generality and modularity of the polymer backbone, we sought to incorporate other recognition elements within the universal scaffold. As such, hydrogen-bonding functionalities were of interest, owing to the high density of well-established supramolecular motifs based upon hydrogen bonding (*vide supra*). Prior to our work, Gibson introduced THY-functionalized norbornenes as ROMP-accessible scaffolds that afforded well-defined polymers.[50] Additionally, Rotello

introduced the ROMP of DAP-functionalized norbornenes that self-assembled with uracil into polymersomes.[39]

With the established studies of Gibson and Rotello, we investigated the installation of DAT and DAP groups within the norbornene scaffold (Figure 3a,b).[51,52] ROMP of a DAP-functionalized *exo*-norbornene proceeded without being impeded by self-aggregation or catalyst interference.[51] The ROMP of the DAT-functionalized *exo*-norbornene can be achieved; however, the resulting polymers immediately precipitated, owing to self-association. Polymerization in the presence of *N*-butylthymine circumvents the aggregation of DAT moieties and is considered an effective supramolecular protecting group strategy,[23,53] because unwanted noncovalent interactions are suppressed. Further studies utilizing the DAP-based poly(norbornene) revealed the ability to template the polymerization of an analogous THY-based norbornene (Figure 3c).[52] The success of the template approach relied upon exploiting self-assembly: the DAP framework has a low dimerization constant in halogenated solvents ($K_{dim} = 2.6 \pm 0.2$ M^{-1}), coupled with a relative high association constant for the THY substrate. In addition, the templated polymerization proceeds with greater control, echoing the sophistication and fidelity of more complex materials generated by Nature.

Efforts to increase the functionalization methods and thus the applicability and complexity of the UPB led to the incorporation of main-chain supramolecular motifs,[54] generating telechelic supramolecular polymers. Initially spearheaded by Grubbs,[55] ROMP in the presence of chain-transfer agents (CTAs) has been utilized as a prototypical method to install functional moieties at chain termini, while effectively circumventing postpolymerization terminal functionalization. Since then, the ROMP−CTA approach has been applied to synthesize telechelic polymers with complete control over end groups.[56] We have utilized ROMP−CTA to install either
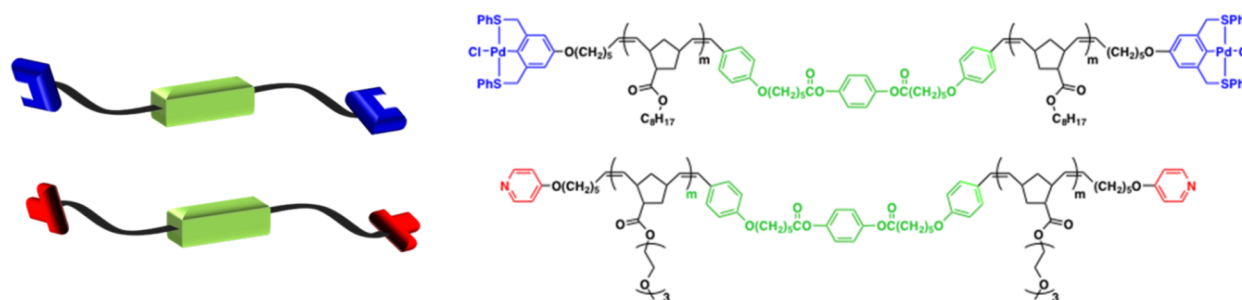
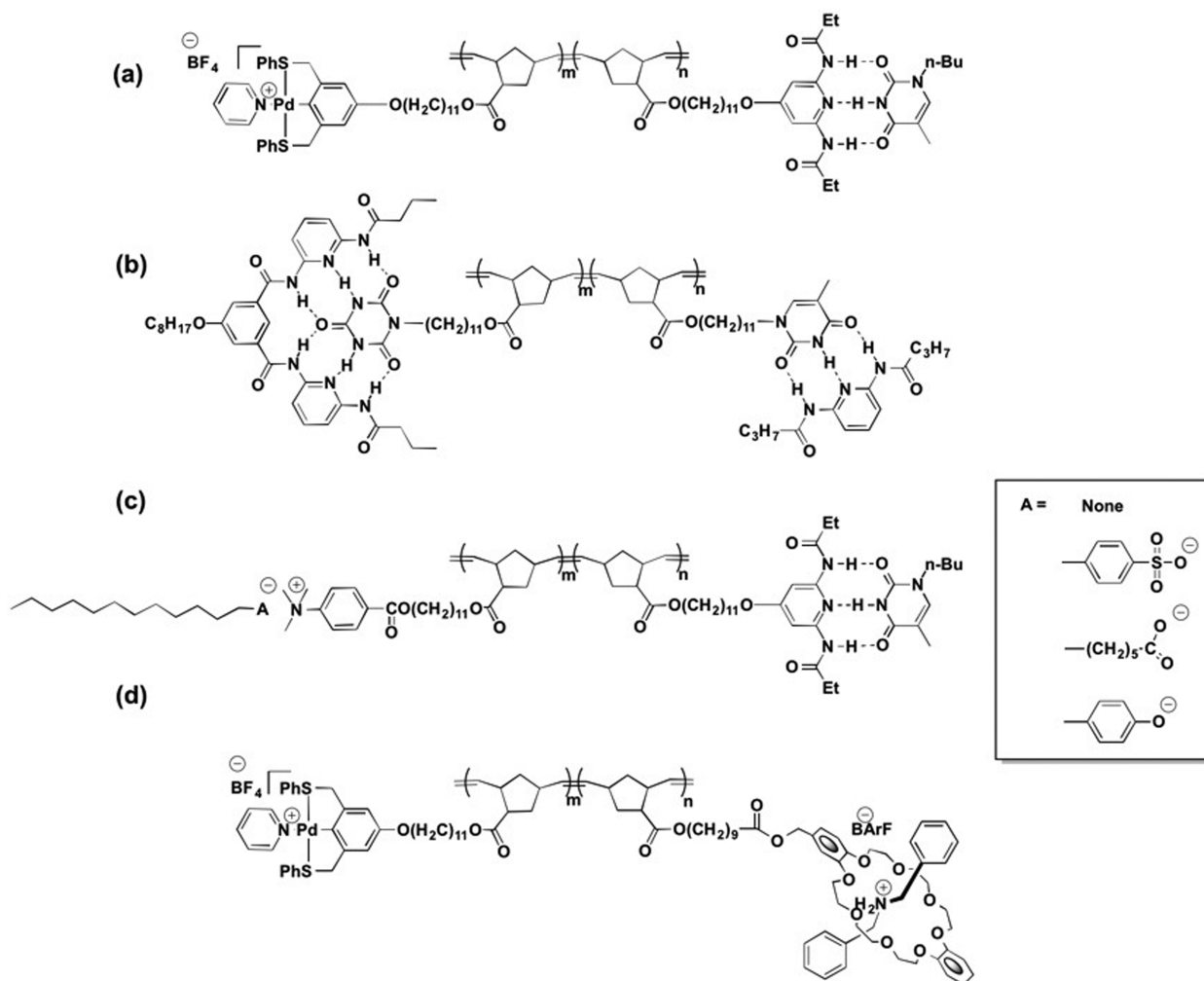**Figure 4.** Homotelechelic polymers prepared using a bimetallic initiator.
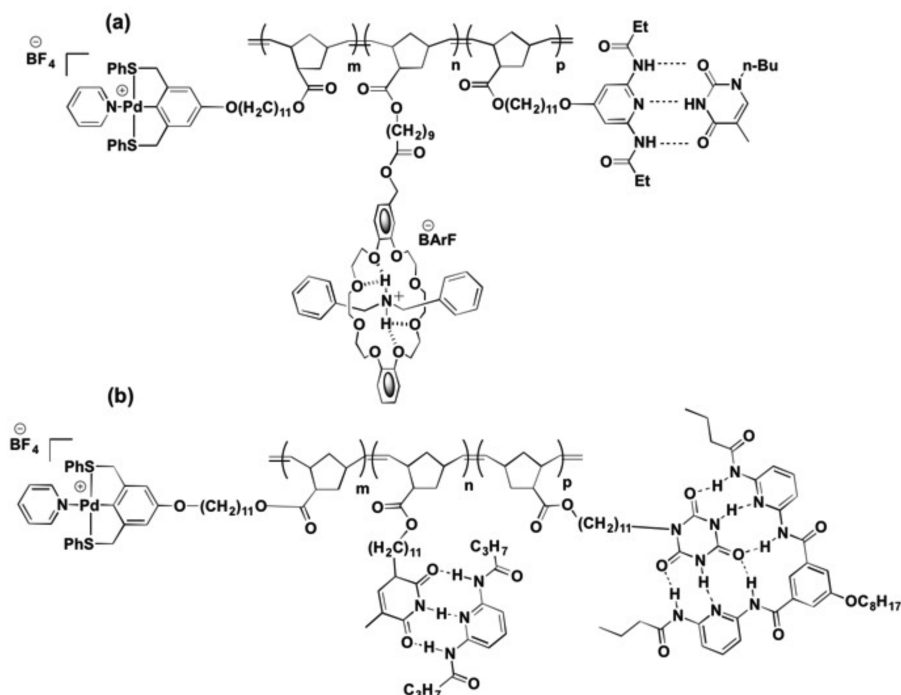

Figure 5. UPB designs with two orthogonal units.

hydrogen-bonding or metal-coordination sites within homotelechelic UPBs that self-assemble to form supramolecular block copolymers (BCPs).[57] The utility of this approach has also been demonstrated by Meijer.[58]

Although highly advantageous, the ROMP–CTA approach is not living and suffers from a lack of control over dispersity.[59] Utilizing the living nature of ROMP to our advantage, we synthesized a bimetallic initiator[60] that conducted the polymerization of norbornenes, wherein the use of a functional chain terminator (CT) installed the supramolecular moieties. Homotelechelic UPBs composed of SCS-Pd^{II} pincer- or pyridine-functionalized termini were synthesized, and subsequent self-assembly into supramolecular alternating BCPs

sustained by (pincer) Pd–N (pyridine) interactions was achieved (Figure 4).[61]

In our preliminary studies, we demonstrated the ability of ROMP to install hydrogen-bonding and metal-coordination units within a variety of functionalized UPBs. Additional studies to increase the complexity of the UPB led to the installation of supramolecular motifs within the main chain. With these studies effectively comprising our "supramolecular toolbox", advanced systems could be pursued that combined our UPB designs, while exploiting orthogonal interactions to generate supramolecular polymers with a high density of functionalization. Indeed, bridging the gap between synthetic and natural systems relies on utilizing multiple functionalization methods in

Figure 6. UPB designs with three orthogonal units.

concert, while exploiting orthogonality to achieve design complexity.

ENGINEERING ORTHOGONALITY WITHIN UPB FRAMEWORKS

Installation of Two Orthogonal Supramolecular Units on the UPB

Prior to our work, supramolecular units had been incorporated onto polymer systems, but few had incorporated multiple distinct noncovalent interactions within a single chain.[62] In 2003, we demonstrated that two orthogonal supramolecular functionalities could be introduced[63] via living ROMP[10] of norbornenes functionalized with palladated SCS-pincer (block A) and DAP units (block B). This afforded <u>AB</u> poly-(norbornene)-based BCPs (wherein each underlined block contains a pendant supramolecular functionality) with two orthogonal pairs (SCS-Pd^{II} pincer−pyridine and DAP−THY) as pendant side chains (Figure 5a). This study, along with orthogonal hydrogen-bonding and metal-coordination pairs on a UPB, exhibited a one-pot self-assembly (Figure 5).[64] Collectively, these UPB systems showcased the functional group tolerance of ROMP, while utilizing a diverse library of supramolecular units.

We introduced a variety of supramolecular units with K_a values differing by orders of magnitude that do not self-associate within our design. Orthogonal hydrogen-bonding interactions included DAP−THY and Wedge−CA, wherein THY or CA were pendant groups on poly(norbornene) (Figure 5b).[65] Additional systems were based on orthogonal DAP−THY and trimethylbenzeneaminium−oxoanion, as well as SCS-Pd^{II} pincer−pyridine and dibenzylammonium−DB24C8 (Figure 5c,d). Self-sorting behavior was demonstrated in the system utilizing two hydrogen-bonding pairs upon addition of a more strongly associating complementary unit.[66]

<u>AB</u> BCPs were prepared in each of the aforementioned cases via living ROMP, independent of supramolecular units on the UPB. Recognition units that are orthogonal to the ruthenium catalysts were incorporated and polymerized in a living fashion. In all cases, self-assembly proved to be orthogonal via a two-step or one-pot addition of hydrogen-bonding or metal-coordination complementary units.

Installation of Three Orthogonal Supramolecular Units on the UPB

We also incorporated three orthogonal interactions within a UPB. The hydrogen-bonding DAP motif was combined with SCS-Pd^{II}−pyridine and DB24C8−ammonium pairs (Figure 6a).[9c] The resulting terpolymer maintained orthogonality, achieving highly specific metal coordination, near-quantitative pseudorotaxane formation, and DAP−THY association. ^{1}H NMR spectroscopic titration studies demonstrated that threading of the pseudorotaxane moieties strengthened the metal coordination through counterion exchange without affecting coordination integrity.[9c]

With the ability to engineer orthogonal self-assembly within UPB terpolymers, we explored combinatorial possibilities of recognition motifs that yielded stimuli-responsive polymers. A supramolecular polymer incorporating the interactions SCS-Pd^{II} pincer−pyridine, DAP−THY, and Wedge−CA demonstrated solvent dependency.[67] Whereas in CH$_2$Cl$_2$ an orthogonal self-assembly was sustained, disassembly of the Wedge−CA motif occurred during metal coordination when 85:15 CH$_2$Cl$_2$/dioxane was used, owing to the weakening of hydrogen bonds in dioxane (Figure 6b).

ENGINEERING ORTHOGONALITY WITHIN SUPRAMOLECULAR BLOCK COPOLYMERS

Orthogonally End-Functionalized BCPs

Whereas hydrogen-bonded supramolecular BCPs have been demonstrated by Meijer[26b] and Bernard,[34] O'Reilly and others[68] have assembled metallosupramolecular copolymers with the ability to fabricate hollow nanocage structures. Efforts
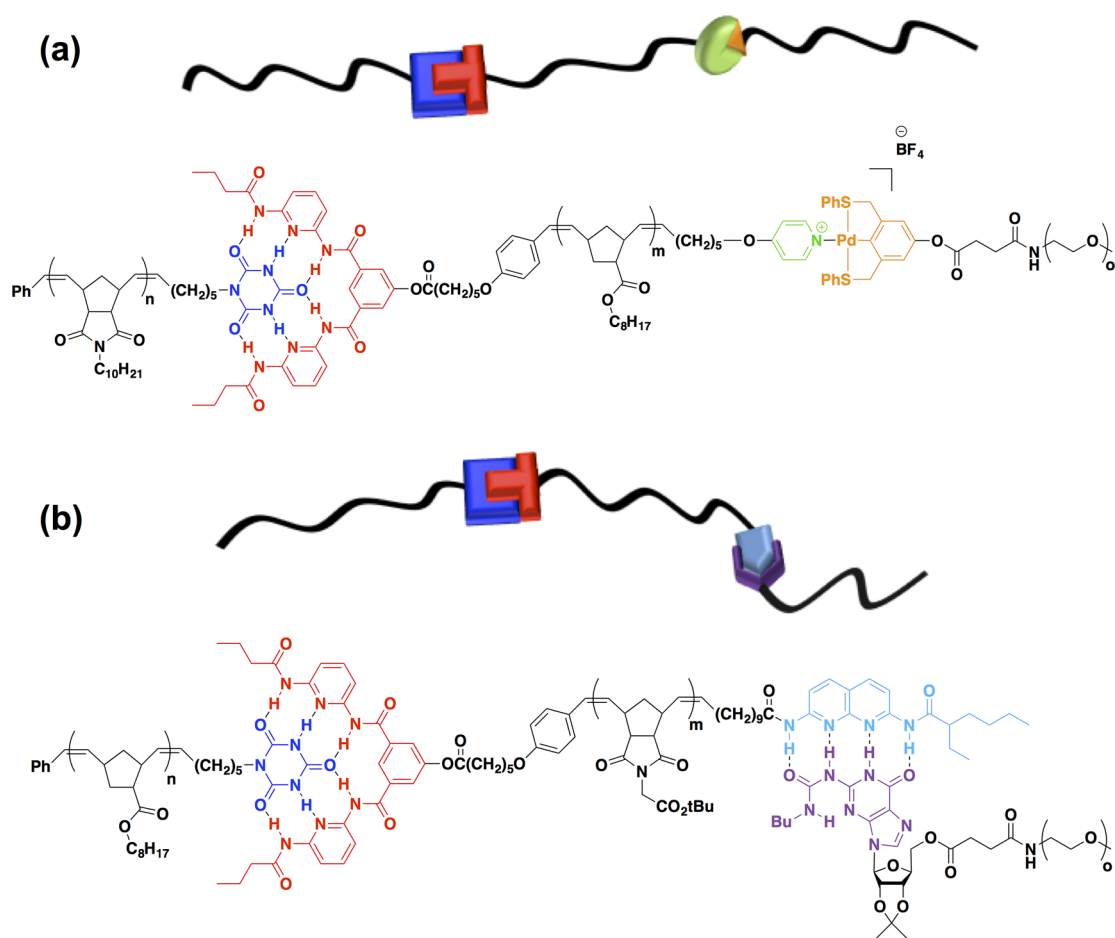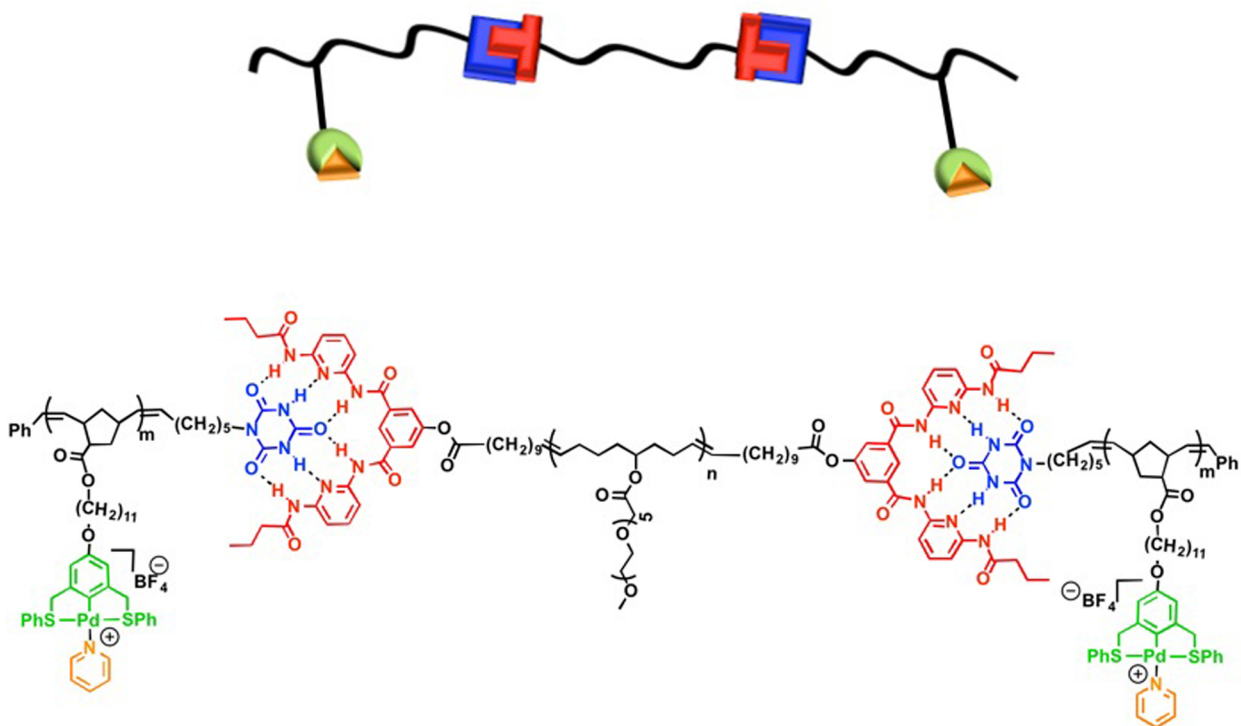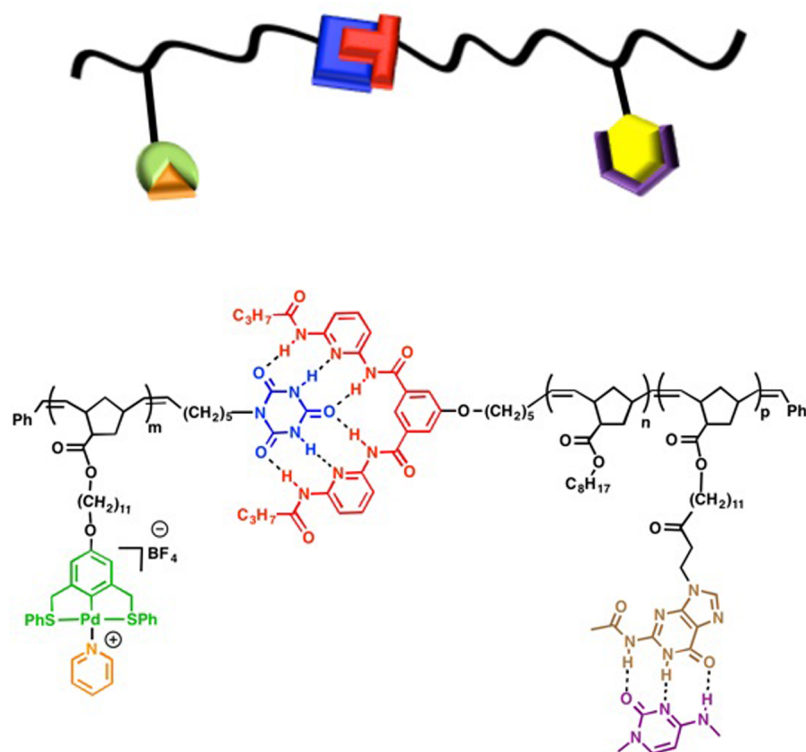
Figure 7. End-functionalized triblock designs.

Figure 8. Schematic depicting mixed functionalization supramolecular strategy.

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Figure 9. Schematic of triblock design with three orthogonal units.

to construct supramolecular triblock copolymers, at best, yielded metallosupramolecular AB/A and AB/C[69] and hydrogen-bonding A/B/A, A/BC, and AB/CD BCPs, with design complexity lying in the variety of blocks utilized.[34]

Challenges associated with preparing heterotelechelic polymers containing recognition units at the initiating (α) and terminating (ω) ends have limited the development of supramolecular BCPs to mainly supramolecular AB diblock and (AB)$_n$ multiblock copolymers.[70] To realize an A/B/C triblock copolymer, a new strategy was needed to install orthogonal supramolecular motifs at the chain ends of heterotelechelic polymers. In 2009, we reported the first synthesis of a main-chain A/B/C triblock copolymer (wherein A/B/C denotes end-functionalized blocks) composed of CA end-functionalized poly(norbornene dicarboximide), an α-Wedge, and ω-pyridine end-functionalized poly(norbornene), and a SCS-Pd^{II} pincer-terminated poly(ethylene oxide) (PEO) (Figure 7a).[14a] Heterotelechelic blocks were achieved using a modified Grubbs initiator that functionalized the α-terminus, while a chain-terminator (CT) installed a second orthogonal functional group onto the ω-terminus.

Covalent BCPs have a tendency to phase separate between incompatible polymer blocks, a fact holding true for supramolecular systems and necessitating the use of recognition units with high enough K_a to hold polymeric chains together.[9,14] One system that fulfills this requirement is the combination of the Wedge−CA and DAN−UG recognition units. Both orthogonal recognition pairs were used to synthesize A/B/C BCPs,[14b] wherein block A was a CA-functionalized poly(norbornene), block B comprised a Wedge and DAN end-functionalized poly(norbornene dicarboximide), and block C was a UG-functionalized PEO (Figure 7b). Complete orthogonality was verified through a combination of ¹H NMR spectroscopic titrations and 2-D NOESY.

Orthogonally End- and Side-Chain-Functionalized BCPs

In line with our conquests to increase design complexity, we uncovered an architectural design that mixed side-chain and main-chain self-assembly.[13] In 2009, supramolecular A/B/A triblock copolymers were successfully synthesized using two previous tools in concert, the UPB design and the modified initiator.[13] In our design (Figure 8), four separate supramolecular units exhibited orthogonality through the use of pendant Pd^{II} SCS-pincer−pyridine side chains on a poly(norbornene) (block A) and Wedge−CA motifs on a functionalized poly(cyclooctadiene) main chain (block B). A functional CTA transfers the orthogonal supramolecular unit of choice to the ω-terminus of side-chain-functionalized block A. ROMP conducted in the presence of a bis-functionalized CTA affords homotelechelic polymers that serve as middle blocks able to undergo main-chain self-assembly with two A blocks.

Installation of Three Orthogonal Supramolecular Units on a Diblock Copolymer

Our final A/B block copolymer design (Figure 9) involved multiple supramolecular recognition motifs.[13] Block A was ω-CA-functionalized poly(norbornene) with SCS-Pd^{II} pincer residues, while block B was an ω-Wedge-terminated poly(norbornene) with pendant guanine groups. The SCS-Pd^{II} pincer coordinated with pyridine-based moieties, while the guanine participated in hydrogen bonding with cytosine. ¹H NMR spectroscopy confirmed that K_a values of the guanine/cytosine and the Wedge−CA moieties differed by 3 orders of magnitude, with both assemblies independent of the metal-coordinating side chains. The main- and side-chain functionalization steps were sequence-independent demonstrating orthogonality throughout the supramolecular polymer.
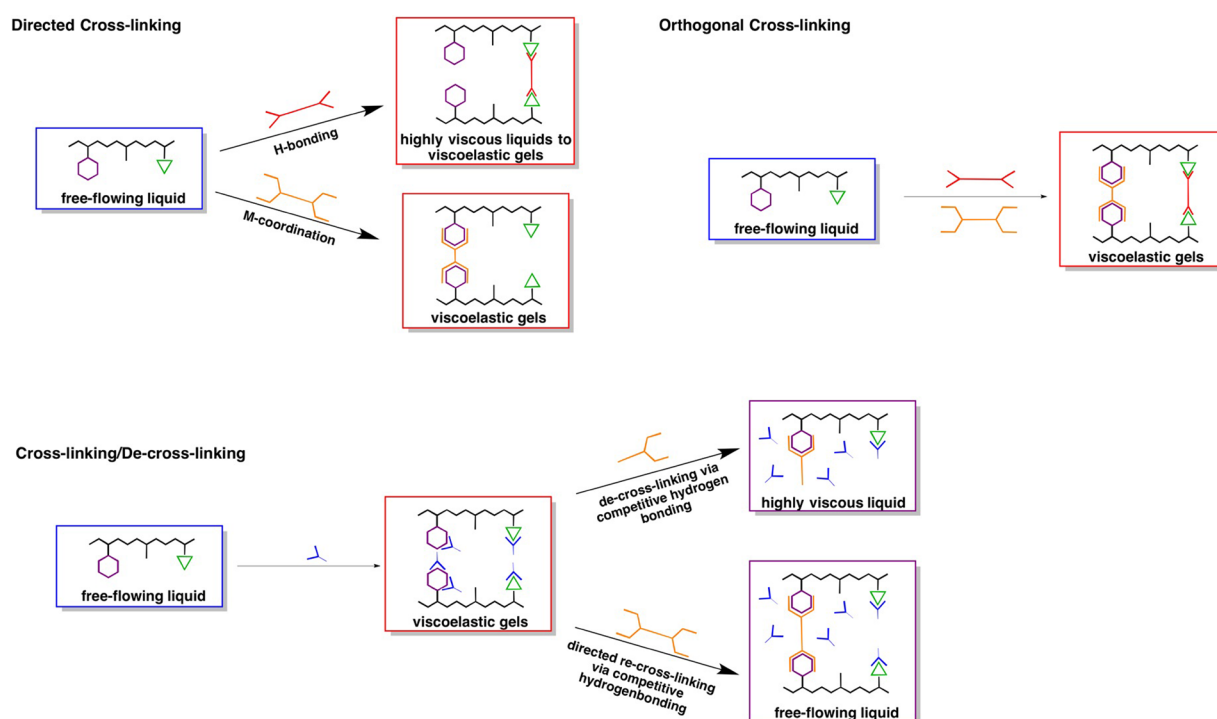
Figure 10. Generalized supramolecular cross-linking and de-cross-linking strategies.

EXPLOITING ORTHOGONALITY VIA SUPRAMOLECULAR CROSS-LINKING

With the ability to control supramolecular assembly by design, we investigated the use of self-assembly to tune macroscopic mechanical properties. The use of supramolecular units as reversible network connectors[71] and compatibilizers has been demonstrated.[44] While cross-linking has historically been achieved via self-dimerization,[23] examples of supramolecular cross-linking have been demonstrated by Craig, Weder, Rowan, and others,[72] wherein one supramolecular interaction was utilized to modulate material properties. With these studies in mind, we sought to controllably fabricate systematic cross-linking through the use of multiple orthogonal interactions.

Initially, we investigated the use of CA- and DAP-functionalized <u>ABC</u> systems, wherein the C block had pendant SCS-Pd[II] pincer motifs. Addition of ditopic Wedge or ditopic THY motifs resulted in cross-linking for the CA and DAP systems, respectively. In both polymers, bis(pyridines) also led to cross-linking (Figure 10).[73] A later design featured two complementary hydrogen-bonding motifs to modify polymer viscosity via cross-linking.[74] Similarly, addition of ditopic DAT or Wedge agents to a UPB with pendant CA and SCS-Pd[II] pincer side chains demonstrated noncovalent cross-linking. The material produced was modulated by the amount of cross-linking agent added and the topicity of hydrogen-bonding motifs affected: Wedge−CA cross-linking increased overall polymer viscosity while CA−DAT cross-linking produced viscoelastic gels. Competitive de- and re-cross-linking of the CA-functionalized UPB also demonstrated the ability to transform polymers from highly viscous to highly elastic materials.[12]

We probed the modularity of these materials via addition of supramolecularly competitive de-cross-linkers (Figure 10).[12a] Wedge−CA units were used in competition with DAT−CA motifs, while SCS-pincer Pd[II]−bis(pyridine) motifs were

disrupted by the addition of triphenylphosphine units. Metallosupramolecular polymers demonstrated increased relative viscosities upon cross-linking,[73] compared with hydrogen-bond-based cross-linking.

TOWARD FUNCTIONAL MATERIALS VIA ORTHOGONAL SELF-ASSEMBLY

As "bottom-up" engineers of noncovalently bound assemblies, the paramount challenge afflicting supramolecular chemists spawns from designing systems that echo synthetic simplicity yet emulate the elegance and complexity of natural biosystems. Supramolecular polymers have been made wherein the molecular recognition event is founded solely upon hydrogen bonding or metal coordination, and the resulting architecture exudes stimuli-responsive,[25,32,75] liquid crystalline,[43] or healable[47] behavior or can been engineered for biological applications (e.g., adhesion,[26a] biotin−streptavidin self-assembly[29]). Furthermore, supramolecularly enhanced dyes,[2,33] semiconductors, and other architectures continue to emerge as functional materials utilizing $\pi\cdots\pi$ stacking as a prominent driving force. Although highly desirable materials have been engineered utilizing nonorthogonal systems, the introduction of complexity relies upon manipulating principles governing orthogonal self-assembly. We have exploited the increased modularity of our design to engineer monolayers on gold surfaces using poly(norbornene)s functionalized with DAP or THY and a poly(4-vinylpyridine)-functionalized bis(pincer) ligand.[76] The orthogonal behavior of DAP−THY and pincer−pyridine interactions was exploited to fabricate multilayered surfaces. Specifically, a gold surface was patterned with a thiol-functionalized DAP using microcontact printing, while 4-mercaptopyridine was used to fill the negative pattern, both interactions being achieved in a site-specific manner with high fidelity. The hydrogen-bonding and metal-coordination do-

mains exhibited individual responses to external stimuli, providing control of assembly in three dimensions.

The concept of orthogonal self-assembly is indeed not foreign in the realm of supramolecular chemistry, with recent reviews highlighting the progression toward more complex supramolecular systems.[6] Clearly, the exploitation of orthogonal directional forces in concert is essential for developing both higher ordered structures and materials.

SUMMARY AND PROSPECTUS

The construction of synthetic materials that rival the complexity of Nature has been tackled mainly via the incorporation of supramolecular units in polymeric systems. In this Account, we have described techniques to achieve high density side-chain-functionalized, homotelechelic, heterotelechelic, and mixed side- and main-chain functionalized supramolecular polymers, with a focus on increasingly complex architectural designs. Our ability to achieve complexity is partially owing to the integration of a variety of supramolecular motifs, while exploiting distinct K_a values to assemble diverse polymeric assemblies. This has resulted in controllable assembly/disassembly upon introduction of external stimuli or additives. ROMP−CTA can be employed individually to afford homotelechelic polymers or in concert with functionalized CTs to generate heterotelechelic polymers. Efforts to exploit polymer properties have also led us to use recognition units as ditopic cross-linkers and de-cross-linkers for the modification of viscoelastic properties. While our preliminary ventures using these complex material designs have led to surface-patterning and viscosity modification, there awaits a bevy of potential applications in which highly modular supramolecular polymer architectures can be showcased to their maximum potential.

Current approaches have spanned the spectrum of top-down to bottom-up design: the push toward developing orthogonally assembled biomimetic polymers will require the pooling of expertise from multiple disciplines to yield functional materials resulting from robust architectural designs. With increasing efforts in exploiting microphase separation behavior of BCPs to achieve self-fabricating materials, it may even be possible to surmise that the future of complex system design to yield complex matter will require only self-fabrication.

Future progress will continue toward multifunctional materials with increased modularity to achieve tasks requiring great synergy. With the push toward novel and sustainable energy sources, complex supramolecular polymeric systems may find application in catalytic or energy-harvesting purposes. Our ability to build increasingly complex and multiresponsive polymeric materials based on Nature's constructs can lead to the study, comprehension, replication, and even amplification of biological processes.

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