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Polymer Chemistry Minireview

Topology, Assembly, and Electronics: Three Pillars for Designing Supramolecular Polymers with Emergent Optoelectronic Behavior

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Abstract "Emergence-upon-assembly" – where unique properties arise following the formation of hierarchical superstructures – is a common strategy employed by biology to produce materials that possess advanced optical and electronic properties. Supramolecular polymers are periodic macromolecules, whose monomers are held together by noncovalent bonding, and they display emergence-upon-assembly when sufficient consideration is given to topology, assembly, and orbital interactions. Herein we discuss the criteria to consider when designing supramolecular polymers with emergent optoelectronic properties by placing particular emphasis on the contributions of topology, assembly mechanisms, and intramolecular electronic communication in donor-acceptor systems.

Introduction

Living systems produce materials with complex structures and useful optoelectronic properties by bringing together simple organic components such that the resulting nanoscale organization triggers new interactions with electromagnetic fields, ions, and charges. Some particularly elegant examples include green fluorescent protein,[1] rhodopsin,[2] and the bacterial reaction center[3-5] that possess order on the molecular and nanometer scale and whose responses to external stimuli include switchable fluorescence, signaling, and conversion of light to chemical energy, respectively. Two noteworthy attributes that these materials share are that they are composed almost entirely of organic matter and possess the characteristic of emergence-upon-assembly – in which new properties are only observed upon the formation of hierarchical order, whose structure across the molecular-to-macroscopic continuum is dictated by noncovalent interactions programmed into the individual molecular components. As a result of this spatial arrangement, new electronic interactions arise that enable remarkable functionality, such as the conversion of light to chemical energy in photosynthesis (**Figure 1**). Specifically, in the reaction center a series of chromophores with systematically decreasing energy levels are positioned precisely in space to enable a cascade of electron and energy transfer events that rapidly move photogenerated charge from one side of the complex to the other.[3-5] Current synthetic routes are unable to reproduce such multi-lengthscale order and advanced function with artificial materials because the large sizes and the complex assembly processes involved exceed the limits of modern manufacturing capabilities. Despite the prevalence of the elegant and functional optoelectronically active structures found in Nature, the materials that continue to dominate the optics and electronics industries are crystalline and inorganic,[6-9] and are not competitive with natural systems in terms of cost, toxicity, and weight, but the drawback of using biomaterials as replacements is that their lack of stability and poor processiblity has precluded their device integration. So for both industrial applications and to gain fundamental insight into the complex machinery of life, it is important to continue developing organic materials that possess hierarchical order and stimuli-responsive optical and electronic behavior.

By adopting a biomimetic design approach[10-12] where hierarchical assembly and emergent behavior are equally important goals of molecular design, researchers have successfully developed organic materials with impressive optical,[13] mechanical,[14,15] and electronic properties.[16] Building blocks of both biological[17-20] and synthetic origin[10-12] have been leveraged to achieve diverse molecular architectures and functions, and the common element among all these components is that reversible, noncovalent bonding directs superstructure formation. A particularly noteworthy subset of these bioinspired materials, and the subject of this minireview, are the supramolecular polymers,[21-23] which are macromolecules whose monomers are held together principally by noncovalent bonding through either H-bonding, $\pi\cdots\pi$ stacking, metal coordination, or mechanical bonding (**Figure 2**).[24-27] Like oligonucleotides and oligopeptides, they combine the benefits of polymer chemistry and supramolecular chemistry to achieve properties that are absent in the individual components. The benefits of supramolecular polymers include their ease-of-preparation from simple building blocks, dynamic macromolecular composition, and hierarchical structure. The remarkable new emergent properties can include the ability to embed information within molecular scaffolds,[28,29] impressive mechanical performance, [4,15] structural changes in response to biological stimuli,[30-32] and beneficial interactions with electromagnetic fields.[13] Thus, many compelling reasons exist to continue developing new supramolecular polymer-based solutions to address pressing research challenges.

Supramolecular polymers have been explored in the context of medical, electronic, energy, and environmental applications, and several excellent reviews exist already related to this rapidly growing research field.[16,21-23,31] Rather than providing another comprehensive article, our aim is to highlight a few exemplary supramolecular polymers and related systems that achieve one particularly important photophysical property, namely photoinduced charge separation, which is a critical step in artificial photosynthesis.[33] By highlighting their commonalities, we hope to derive design principles for creating new organic materials for energy harvesting, signaling, and sensing. Supramolecular polymers with emergent optoelectronic properties are achieved when considerable attention is given to the three pillars of photoactive supramolecular polymer design, which are topology, noncovalent assembly, and electron and spin dynamics. This minireview will discuss the design of artificial supramolecular polymers with emergent optoelectronic properties, where the three aforementioned criteria have been successfully employed to create materials that collect photons and convert them to charges that can be subsequently collected. Particular attention is devoted towards a multicomponent supramolecular polymer prepared in our group composed of a diketopyrrolopyrrole (DPP) electron donor and a perylene derived bisdiimide (PDI) electron acceptor that, following assembly into superstructures with a 2:1 donor-acceptor ratio, produces long-lived charge carriers following irradiation with visible light. [34,35]

Polymer Topology

Macromolecules are distinct from their small molecule counterparts in that their structures are defined not so much by the relative positions of a few atoms in space, but by the sequence and arrangement of molecular repeating units, termed monomers. Thus a major advantage of polymer chemistry is that vast topological diversity is accessible from a few easy-to-prepare building blocks, and that important rheological, mechanical, and electronic properties are dependent on the topology that can be varied by changing reaction conditions during the polymer synthesis. In the context of macromolecular science, the term topology refers to the size, shape, and connectedness as the chief elements of topology.

This includes the monomer sequence of polymer segments, and the accessibility of different polymer topologies is related intimately to the types of bonding that link together monomeric units within a given chain. As such, we suggest that macromolecular topologies can be broadly classified in terms of the bonding types that they employ, which include the *covalent polymers*, *supramolecular polymers*, and *hybrid polymers*, the latter of which use a combination of covalent and noncovalent bonds to arrange monomers spatially.

Polymers whose chains are held together solely by covalent bonds constitute the largest class of synthetic macromolecules, and in *covalent polymers* (**Figure 3a**) topology is dictated by the monomer sequence, the structure of the initiator, and the monomer type. Generally, the covalent polymers are composed of sections of linear chains, whose monomers can be identical or varied, and in the latter case can be arranged along the strand in blocks or as a random arrangement of monomers in the chain. By using initiators with multiple reactive sites, other topologies with different connectivities, such as star polymers,[36,37] can be obtained, and when more than one polymerizable group is incorporated into the monomers, cross-linking between chains occurs. The creative combination of these three elements can lead to more exotic topologies, such as comb,[38,39] dendronized,[40,41] and bottle-brush polymers,[42,43] where initiators themselves can be macromolecules. While there have been significant recent developments related to self-immolative polymers [44-46] and polymers with mechanically labile bonds,[47,48] the bonds within covalent polymers are generally considered to be kinetically and thermodynamically stable under normal laboratory temperatures and pressures. Thus to predict the structure that will be formed during a covalent polymerization, the rate constant k of the reaction employed to make the polymer is the single most useful parameter for predicting chain length, monomer sequence, and even connectivity.

The defining characteristic of *supramolecular polymers* that distinguishes them from covalent polymers is that the monomers in supramolecular polymers are held together by dynamic bonds. These include H-bonding,[49] $\pi\cdots\pi$ stacking,[50] host-guest encapsulation,[51] and any additional interactions where an equilibrium can be established between bound and unbound states. This fluctuation endows supramolecular polymers with a high degree of internal order and adaptability, where shape and chain length can be altered in response to environmental changes. As a result, supramolecular polymers have been explored in the context of shape memory materials,[52] degradable plastics,[53] drug delivery,[28,54] and artificial photosynthetic systems.[55] The use of supramolecular polymers for artificial photosynthesis will be discussed in detail in following sections. The dynamic properties of supramolecular polymers, including degree of polymerization, connectivity, and assembly mechanism, can be understood through the equilibrium constant, K, between bound and unbound states, which captures simultaneously bond strength and equilibrium position. Thus one helpful way to distinguish covalent and supramolecular polymers is that the structure of the former is predicted using k, whereas the behaviors of the latter are conceptualized through K.

The topologies accessible with supramolecular polymers are closely dependent upon the types of interactions bringing the monomers together and are distinct from those common to covalent polymers (**Figure 3b**). Most, but certainly not all, supramolecular polymers employ only a single type of noncovalent interaction to bring the monomers together into repeating chains. For example, monomers where π•••π interactions are dominant form one dimensional stacks,[50] where the polymer chain propagates orthogonal to the plane formed by the aromatic monomer. An alternate architecture is the main-chain or daisy-chain, where propagation is along the long-axis of the monomer, and these polymers typically use H-bonding, metal-coordination, or pseudocatenation to create the polymers.[56] Biological systems rarely use only a single noncovalent interaction, and more sophisticated supramolecular polymer topologies can be obtained when monomers are designed such that multiple noncovalent interactions operate in concert to control the architecture. Although such systems are challenging to design and understand, they often display impressive functionality and can also be used to understand the subtleties of assembly in complex natural materials. An early example is the Amphiphilic nanowire system of Stupp et al.,[56] which uses combinations of H-bonding and van der Waals forces to form multifunctional nanotubes that have been used for numerous applications, such as spinal cord lesion repair in paralyzed animals.[58] Another system uses both H-bonding and π•••π stacking to form supramolecular polymers composed of electron donors and perylene bisdiimide electron acceptors to create multicomponent homochiral donor-acceptor helices that undergo photoinduced charge separation only after the donors and acceptors arrange into a precisely defined topology dictated by the multiple noncovalent interactions acting together.[35,59] Thus researchers are increasingly incorporating lessons from Nature to create supramolecular polymers with progressively more complex topologies, which are making macromolecules with emergent properties more widely available.

A particularly interesting and underexplored class of synthetic materials are the *hybrid polymers*[60] that possess elements of both covalent polymer and supramolecular polymer within a single macromolecular structure (**Figure 3c**). A biological example of such a hybrid polymer system is DNA, which possesses a covalent poly(deoxyribophosphate) backbone and uses the H-bonding and $\pi\cdots\pi$ stacking between purines and pyrimidines orthogonal to the backbone long-axis to cross-link the covalent chains.[61] This synergistic combination of covalent and supramolecular segments is the hallmark of biopolymers, and endows oligonucleotides, oligopeptides, and oligosaccharides with their information-carrying potential. Several groups have attempted to reproduce this hybrid topology – in which supramolecular interactions are used to cross-link covalent chains of non-natural origin – using H-bonding,[62,63] metal coordination,[64,65] donor-acceptor,[66-68] and host-guest interactions.[51,69,70] Some particularly elegant examples have used this cross-linked hybrid architecture to append noncovalent recognition units into a sequence along the polymer backbone as a demonstration of biomimetic chemical information storage.[28] Another noteworthy hybrid architecture involves linear covalent segments with noncovalent recognition units appended to the chain termini, so the hybrid polymers form when these supramolecular macromonomers are brought together, and the resulting polymers make excellent stimuli responsive and degradable materials.[71] Another class of unique topologies that demonstrates the potential of combining covalent and supramolecular polymers is the mechanically bonded polymers – polymers whose monomers are interlocked, thereby preventing dissociation without cleavage of an internal covalent bond. These can include polycatenanes[72,73] and polyrotaxanes,[74-76] whose formation is first templated by noncovalent interactions that bring the monomeric components into a defined conformation followed by the formation of a covalent bond that irreversibly links the components into the chain-link structure. New hybrid topologies are being developed constantly, and what is most interesting about these materials is how they leverage both k and K to produce structures that respond to external stimuli.

Supramolecular Polymer Assembly

In the context of supramolecular polymers, the term "assembly" refers to the step-by-step process by which the monomers come together to form higher order aggregates, and this process is analogous to the polymerization mechanism for the formation for covalent polymers.[77-80] In contrast to covalent polymers, however, supramolecular polymers are held together by dynamic bonds that are constantly traversing the energy landscape between bound and unbound states.[81] As such, important parameters like polymer size and stability at thermodynamic equilibrium are multivariable functions dependent upon concentration, temperature, bond strength, mechanical actuation, and other reaction conditions,[79] so emergent properties and structural changes in response to external stimuli are dictated by the assembly pathway, the strength of bonds that are in continuous flux, and changes to the external environment. While there are many different pathways by which the monomeric building blocks can come together to form higher order structure, three assembly paradigms, namely isodesmic,[80] cooperative,[82,83] and sergeants-and-soldiers[84,85] assembly will be discussed, with particular emphasis placed upon how each contributes to the emergence of chirality – which is the spontaneous formation of axial, helical, or planar chirality that arises from the relative arrangement of the monomers within the supramolecular polymers in the presence of some enantiomeric excess. Emergent chirality is not necessarily present in supramolecular polymers, even if the monomers possess stereogenic units, and as such, monitoring for the emergence of chirality is a powerful technique for assigning the structure, tracking the assembly mechanism, and determining how bond-strength changes as a function of polymerization conditions.[22]

Isodesmic assembly implies that binding strength between monomers is independent of the supramolecular polymer's degree of polymerization,[79,80] and that even in the presence of enantiomerically pure monomers, emergent chirality does not arise.[34] The central assumption behind isodesmic assembly is $K_{\mathrm{n}} = K_{\mathrm{n-1}}$, where n is the number of monomers in the supramolecular polymer and K_{n} is the binding constant for the addition of another monomer to the chain. Thermodynamic parameters including K_n, ΔG^o, ΔS^o, and ΔH^o can be determined quantitatively by fitting titration data to well-known isodesmic binding models.[83] The main implication of isodesmic assembly is that no additional information is communicated between the monomer and polymer that is not communicated by the individual monomers, or in other words the polymer structure does not possess any additional order that is not present in the simplest unit (**Figure 4a**). The increase in size of isodesmic polymers with increasing concentrations is similar conceptually to the increase in degree of polymerization over time in condensation polymerizations because large isodesmic polymers are obtained from small nuclei combining to form longer chains.[78] As a result, in isodesmically assembling supramolecular polymers, emergent chirality does not occur because this requires communication between monomers in the growing chain, which would imply that the binding constant changes as the chain grows because new interactions occur in the chain that are not present in simple dimers. In the example of π•••π stacked linear supramolecular polymers composed of an enantiomerically pure solution of monomers, the resulting chain will be disordered with no preferred orientation of the monomers with respect to the propagation axis of the chain. It should be noted that the majority of supramolecular polymers grow according to an isodesmic model.[79]

In cooperative assembly structural information is communicated through the polymer, affecting both the structure of the growing polymer and the strength of binding of each additional monomer.[79,82,83] The defining characteristic of cooperative assembly is that $K_{\mathrm{n}} \neq K_{\mathrm{n-1}}$, in other words the size of the stack affects the binding affinity.[34,78,79] Cooperative interactions can be both positive and negative, where the former increases the binding strength of each additional monomer to growing the chain ($K_{\mathrm{n}} > K_{\mathrm{n-1}}$), and the latter occurs when each additional monomer binds less strongly to the growing chain ($K_{\mathrm{n}} < K_{\mathrm{n-1}}$). Many different types of cooperative pathways have been proposed to accommodate for the different origins of cooperativity, so no standard model exists for determining thermodynamic parameters for binding in cooperative supramolecular polymers, however most positively cooperative supramolecular polymer assembly pathways share common attributes: firstly, the relationship between chain size and concentration is termed "nucleation growth" and is almost the exact opposite to the growth of chains over time in a living polymerization. Unlike living polymerizations, the oligomerization of the monomers, termed nucleation, is initially slow, but once initiation occurs, polymerization proceeds rapidly. Nuclei form until the number of monomers reaches a threshold value, after which they propagate into long chains through a pathway referred to as elongation (**Figure 4b**).[78] A second common attribute of positively cooperative polymer assembly is the emergence of higher order chirality when a chiral monomer is present in excess. One example of this phenomenon has been observed in π•••π stacked heteroaggregates composed of achiral PDI electron acceptors and chiral DPP electron donors, whose individual components form π-stacked homoaggregates without emergent chirality.[35] When both components are mixed, they form 2:1 donor:acceptor heteroaggregates as a result of π•••π stacking and complementary triple H-bonds between the donor and acceptor. What is remarkable about these systems is that, in isolation, the chiral donors do not display emergent chirality, but when the chiral donor is mixed with the achiral acceptor, homochiral helices form because of the cooperative interactions of the donors and acceptors in the growing stacks, and as the stack grows, so too does K for the binding of additional monomers. [34] An important consequence of this cooperative assembly is that the association of the monomers into supramolecular polymers can be observed by simply monitoring the emergence of chirality as degree of polymerization increases, a phenomenon that is absent in the supramolecular polymers formed from either of the individual components.

A final use of emergent chirality to understand assembly and structure in supramolecular polymers involves the sergeants-and-soldiers principle. In the sergeants-and-soldiers assembly pathway, a small percentage of chiral monomers impose chirality onto an achiral supramolecular polymer.[84,85] This small enantiomeric excess directs the rest of the otherwise racemic mixture of chains to follow the directionality imposed by the chiral building block (**Figure 4c**). In terms of understanding structure and assembly, there are several important implications of the sergeants-and-soldiers principle: firstly, the resulting chiral structures are easily studied by a variety of accessible analytical tools. Secondly, the revelation of emergent chirality confirms that cooperative interactions are driving assembly, and this would be difficult to confirm in the absence of emergent chirality. Finally, the ability of a small stimulus, in this case nominal enantiomeric excess, to control structure and emergent properties suggests many opportunities remain to use supramolecular polymers as sensors and reconfigurable materials.

Emergent Optoelectronic Properties

Photosynthesis is an inspiring natural model for the design of artificial materials to convert light directly to charge and thereby source infinitely renewable energy to meet increasing global demand.[86] The components of photosynthesis are remarkable in that they are organic, they organize into complex arrangements as a result of multiple noncovalent interactions operating in concert, and the directional flow of energy and electrons occurs as a result of the synergistic combination of structural and orbital effects. Increasingly, researchers are attempting to create organic systems for artificial photosynthesis,[33] where successful materials achieve long-lived charge-separated states by bringing together electron donor and electron acceptor components into structures that possess the precise spatial arrangement, orbital energies, and electronic coupling to facilitate photoinduced electron transfer with long-lived charge separated states. Supramolecular systems, and particularly supramolecular polymers, are ideal for artificial photosynthesis because they can achieve complex topologies with the requisite long-distance order from easy-to-prepare and modular components that come together as a result of noncovalent assembly. By appropriately designing topology, assembly, and spin and orbital interactions, a number of artificial systems have been prepared that successfully produce long-lived charge separated states following photoinduced charge separation.

The benefits of synergistically designing supramolecular assembly and orbital interactions to achieve photoinduced electron transfer in solution are elegantly demonstrated in a system designed by Guldi *et al.* composed of guanidinium bis-porphryin donors and fullerene carboxylate acceptors that form a donor-acceptor hybrid (**Figure 5a**) through the cooperation of H-bonding and $\pi\cdots\pi$ stacking.[87] The combination of fullerenes and porphyrins for artificial photosynthesis is an attractive one because of their large abundance and relatively low productions costs, and the charge separation and charge recombination of this pair has many similarities to natural photosynthetic systems, including the ultrafast formation of a long-lived radical pair state. As such both have been explored in the context of bulk heterojunction organic photovoltaics, which consist of blended films of the two components, but the phase segregation has been cited as one of the reasons why device efficiency remains low. Alternatively, covalently linked donor-acceptor systems for artificial photosynthesis with the same two components had been demonstrated previously,[88] but their preparation is cumbersome, which precludes optimization because of the challenges of modifying their structure. In the supramolecular porphyrin-fullerene system, the H-bonding, $\pi\cdots\pi$ stacking and electrostatic interaction work cooperatively to bring the donor and acceptor together in the requisite proximity for electron transfer. The energy level of the donor is positioned such that the singlet excited state undergoes rapid-electron transfer to the donor, and as a consequence, the donor and acceptor undergo efficient photoinduced electron transfer following supramolecular assembly. Although it does not form a supramolecular polymer, this system demonstrates how cooperative noncovalent assembly and appropriate orbital design can be combined to achieve long-lived charge separated states as an emergent property. A binary donor-acceptor co-crystal composed of dibenzotetrathienocoronenes (DBTCCs) and fullerene molecules developed in the Nuckolls group

(**Figure 5b**) forms sandwich-like supramolecular polymer topologies[89] and has been reported to achieve a long charge separated lifetime with high power conversion efficiency.[90] This system makes extensive use of the contorted conformations of DBTCC molecules to envelop the much larger C_{60} molecules in a tight shell. While not supramolecular polymers, the Guldi and Nuckolls systems elegantly demonstrate how energy levels and supramolecular interactions can be designed synergistically. By understanding how these supramolecular systems achieve photoinduced charge separation in solution and in the solid state, respectively, researchers can create supramolecular polymers that combine emergent photophysics with the benefits of macromolecular science.

To this end, a multicomponent helical supramolecular polymer designed by Würthner *et al.* (**Figure 5c**) demonstrates how advanced principles of macromolecular topology and orbital design can be combined to create materials for artificial photosynthesis.[59] In their “coassembled p-n junction” electron donating chiral oligomeric phenylene vinylene (OPV) and PDI electron acceptors are brought into proximity by triple H-bonding between diaminotriazine groups on the OPVs and the diimide groups on the PDIs, forming supramolecular polymers with a 2:1 donor:acceptor ratio. Orthogonal to the H-bonding, homo $\pi\cdots\pi$ stacking between the separate chromophores resulted in a right-handed helix. Upon aggregation followed by photoexcitation with 455 nm light, this system undergoes ultrafast photoinduced charge separation because, like the aforementioned system, the frontier molecular orbital levels are situated appropriately to enable electron transfer from the donor to the acceptor. In an effort to explore a similar multicomponent supramolecular polymer motif, the Braunschweig group developed a system composed of DPP electron donors and PDI electron acceptors (**Figure 5d**), whose superstructure formation is driven by triple H-bonding between a diamidopyridine group on the DPP and the diimide groups on the PDI, as well as homoaggregation from $\pi\cdots\pi$ stacking along the helical axis.[34,35] The advantage of this system is that DPP has been heralded as a promising chromophore for OPVs because its absorption has broad overlap with the solar spectrum,[91] so it has greater potential for energy harvesting, and as a result of strong homo $\pi\bullet\bullet\bullet\pi$ interactions, forms well-ordered aggregates. In addition, the DPP frontier molecular orbital levels are positioned to enable LUMO to LUMO electron transfer or HOMO to HOMO hole transfer to the PDI acceptors, and as expected, upon excitation with 435 nm light, rapid charge separation (<0.2 ps) occurs followed by slower (32 ps) recombination to the ground state. Both these systems demonstrate how supramolecular polymer assembly in combination with appropriate orbital design can be used to achieve photoinduced charge separation. These two examples by Würthner and Braunschweig, demonstrate the potential of combining the benefits of organic chromophores and supramolecular architectures to achieve charge separation in where order and electronic structure can be maintained over large distances.

The Wasielewski group has investigated numerous covalent and supramolecular systems to understand how orbital energies and spin dynamics can be leveraged to increase charge separation efficiency,[55] and in particular have pioneered the use of PDIs as both chromophores and as supramolecular building blocks in artificial photosynthetic systems. Using the same DPP-PDI donor-acceptor pair that was shown to undergo efficient charge separation by Braunschweig *et al.*,[35] they recently demonstrated[92] microsecond charge carrier lifetimes in a covalently linked DPP-PDI donor-bridge-acceptor molecule (**Figure 5e**). Photoexcitation in solution results in quantitative charge separation with a recombination lifetime of 340 ps. However upon forming films, the charge recombination lifetime increases to 4 μs as a result of $\pi\cdots\pi$ stacking in the solid-state. The authors attribute this increase to diffusion of the free charge carriers through the film, and stipulate that these remarkably long lifetimes could lead to efficient charge collection. The Wasielewski system is a unique addition to the donor-acceptor supramolecular systems discussed previously.

Certainly, many more interesting examples exist where supramolecular aggregation and photophysics contribute to the ability to convert light-to-charge, but these examples have been selected to show the evolution of ideas and how the interplay of concepts from supramolecular polymer chemistry and photophysics are leading to new solutions for addressing the challenge of harnessing solar energy. It is critical to emphasize that the emergent optoelectronic behavior discussed in this article is a direct product of careful design that considers the three pillars of supramolecular polymer assembly. Such behavior is readily obtainable after defining a desired topological model, choosing the proper assembly model to yield the target architecture, and matching electronic and spin dynamics of the monomers.

Conclusions

In seeking to develop new materials for optical and electronic applications, researchers are increasingly looking to Nature for inspiration, and in doing so have found that new and useful properties often emerge when multiple components come together into sophisticated macromolecular architectures as a result of distinct noncovalent interactions operating in concert. The exploration of these new materials has led to the realization that molecular topology and optoelectronic properties are intimately related, and that the topologies accessible are dependent upon the types of bonding that bring the components together. These lessons have been applied to prepare a series of supramolecular systems whose purpose is the conversion of light to charge – the first step in artificial photosynthesis – and the results are supramolecular polymers with ever increasing light conversion efficiency and longer lived charge carriers. These successes point towards the continuing need to investigate supramolecular macromolecules, and particularly in the context of developing materials with exotic and useful optoelectronic properties.

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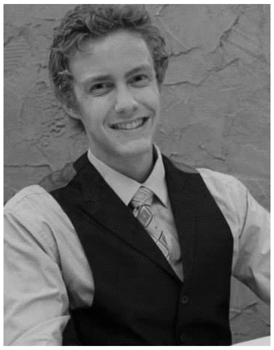

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Figure 1

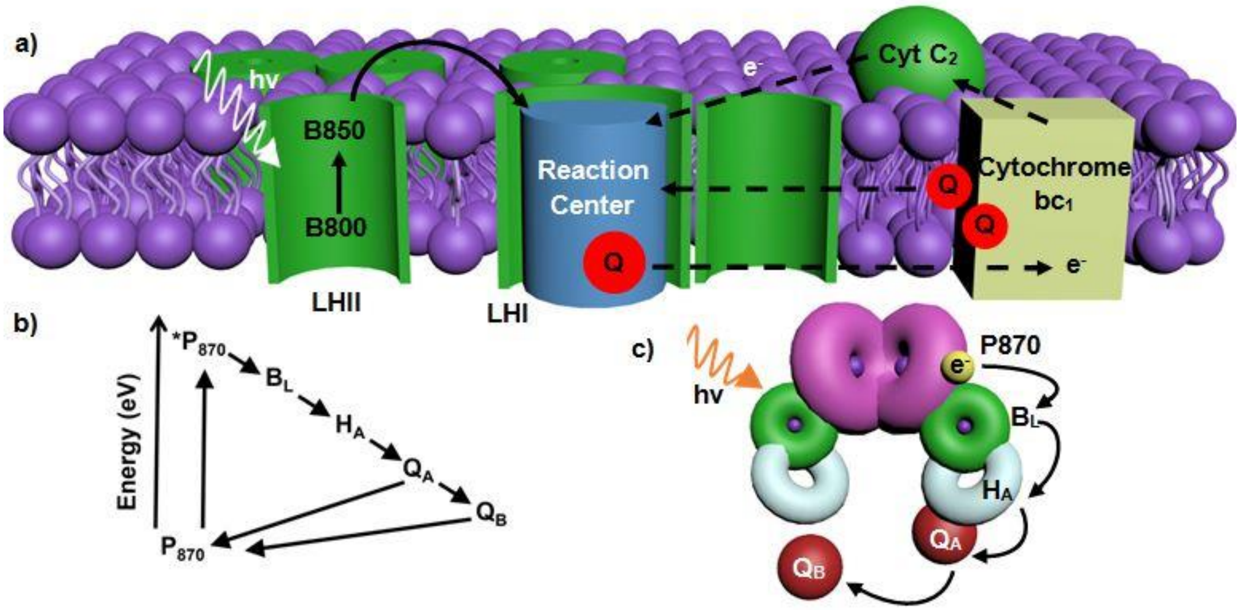


Figure 1. Photosynthesis in *Rhodobacter sphaeroides* light harvesting bacteria. (a) Photosynthesis, the biological process by which incident light is converted to chemical energy, occurs through a complex process involving several optically and electronically active components operating in concert. (b) Directional and fast energy transfer occurs along the chromophores in the reaction center because each step from the special pair to the quinone in the process is energetically favorable. (c) Light for photosynthesis is collected in the reaction center, where energy is passed through a series of precisely positioned chromophores. Incident light (orange) is absorbed by neighboring antenna pigments (purple). Separated charge migrates through the chromophores to a strongly attached quinone (red, Q_A) where it can be abstracted by a neighboring loosely bound quinone (red, Q_B) which diffuses through the membrane to the cytochrome unit where it undergoes oxidation to complete charge separation and transfer.

Figure 2

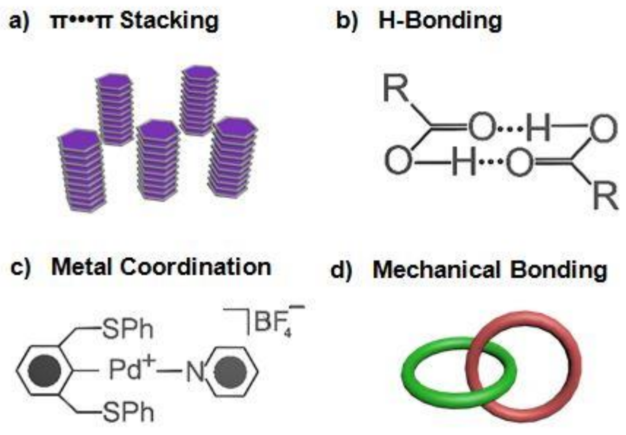


Figure 2. Commonly utilized noncovalent bonding interactions in supramolecular polymer chemistry include (a) π•••π stacking, (b) H-bonding, (c) metal coordination, and (d) mechanical bonding.

Figure 3

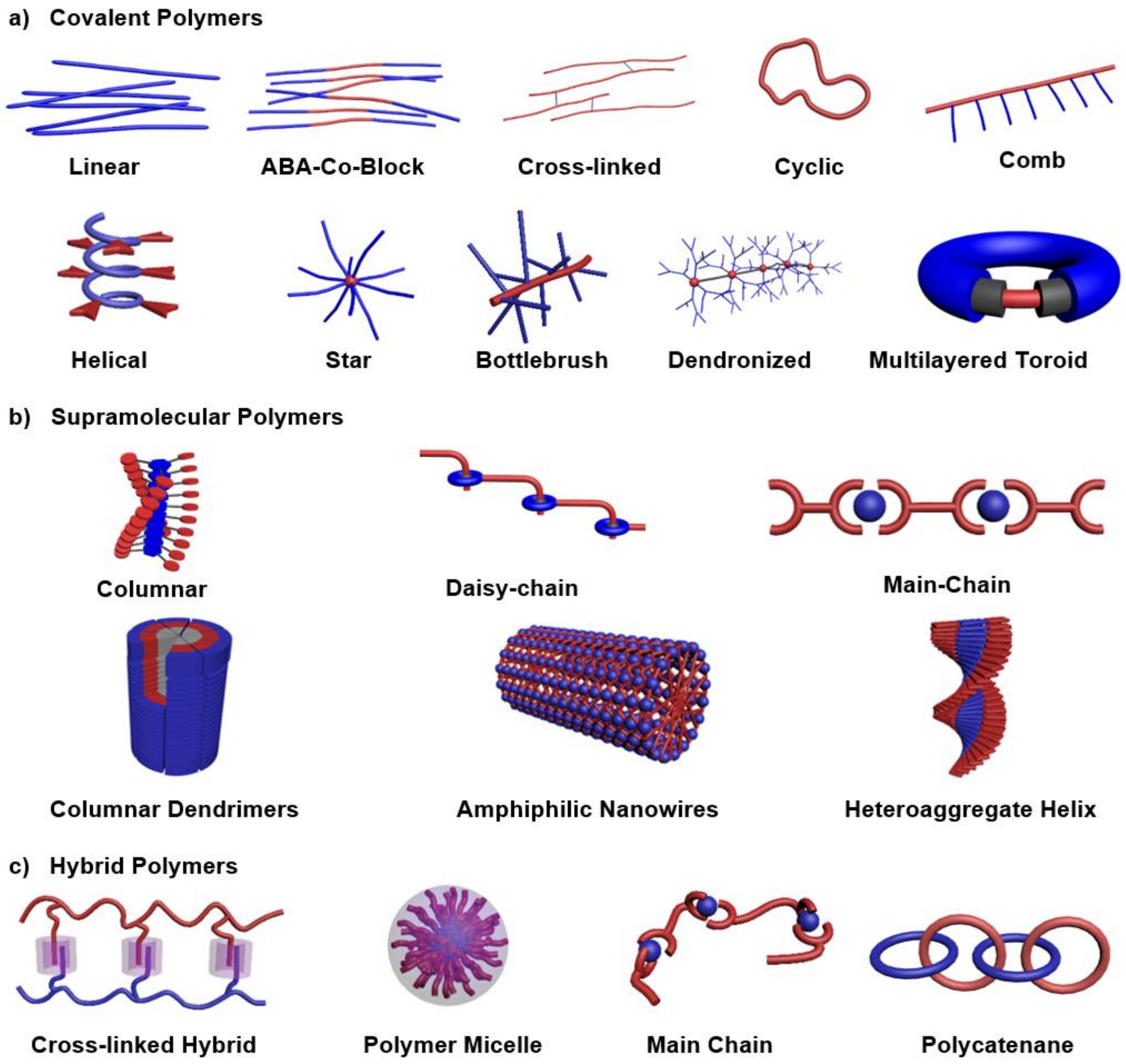


Figure 3. Polymer topology. Polymers derive their properties from the monomer composition, sequence, and arrangement in space (topology). Polymers can be classified in terms of the types of bonding that hold the monomers together, which include covalent, noncovalent, or a hybrid of both. (a) Covalent polymer topologies, where monomers are held together by covalent bonds, are broadly studied in the following categories: cyclic,[93] helical,[85,94] star,[37] bottlebrush,[95,96] dendronized,[40] and multilayered toroid.[97] (b) Supramolecular polymer topologies, where monomers are brought together by noncovalent bonds, are broadly studied in the following categories: columnar,[98] daisy-chain,[99] main chain,[56,100] columnar dendrimers,[101,102] amphiphilic nanowires[57] and heteroaggregate helices.[35,59,103] (c) Supramolecular-covalent hybrid polymers possess functional groups capable

of noncovalent recognition appended to covalent polymers, and are studied in the following categories: cross-linked hybrids,[28,104] polymer micelles,[105]linear hybrids,[56] and polycatenanes.[72]

Figure 4

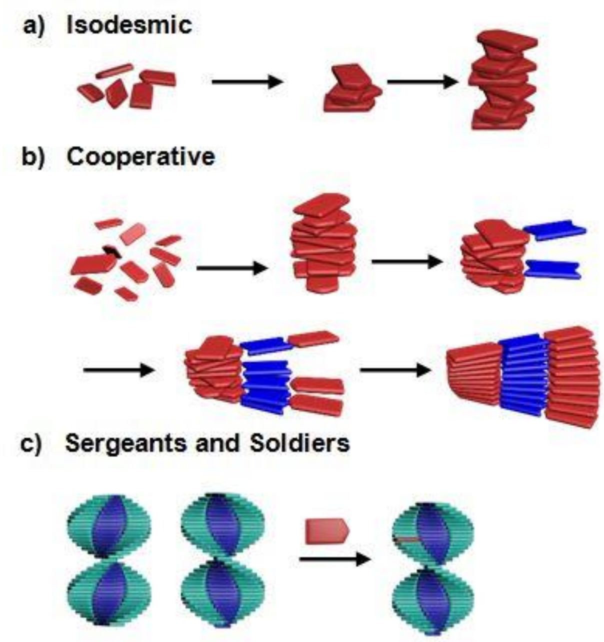


Figure 4. Supramolecular polymer assembly pathways. (a) An isodesmic model assumes equal binding energy independent of stack size, and does not produce emergent chirality. The red shapes indicate chiral monomers. (b) When positively cooperative assembly occurs, the binding strength of new components to the polymer chain increases with increasing stack size as a result of multiple noncovalent interactions operating in concert.[34] Red shapes are chiral monomers that bind to the achiral blue monomers to form a helically chiral superstructure. (c) Sergeants-and-soldiers assembly occurs when a small percentage of chiral component dictates the chirality of a supramolecular polymer.[85] Both green and blue shapes represent achiral monomers, and a small amount of chiral (red) monomer changes the solution from a racemic mixture of *M* and *P* helices to a homochiral solution composed of only *P* helices.

Figure 5

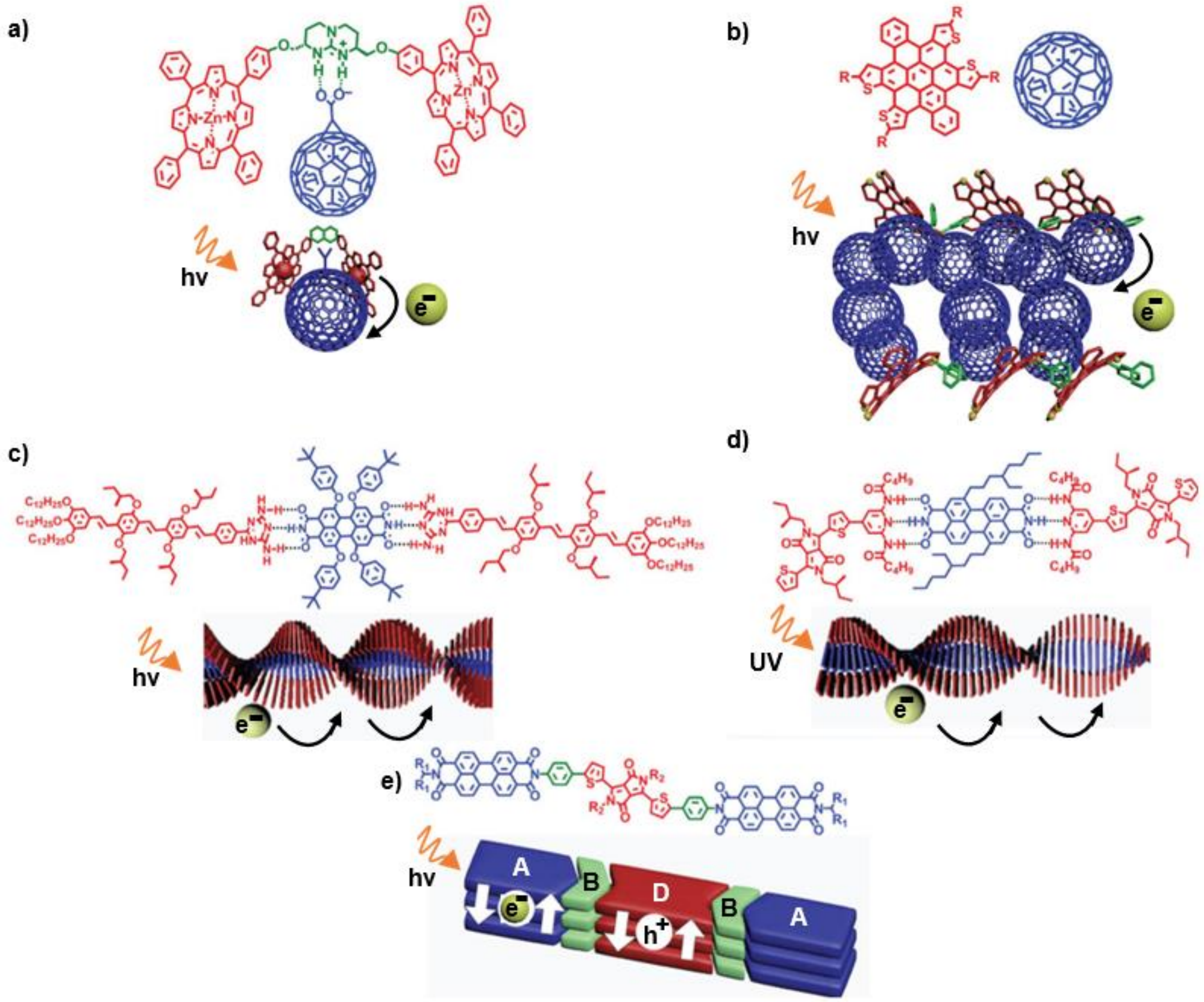
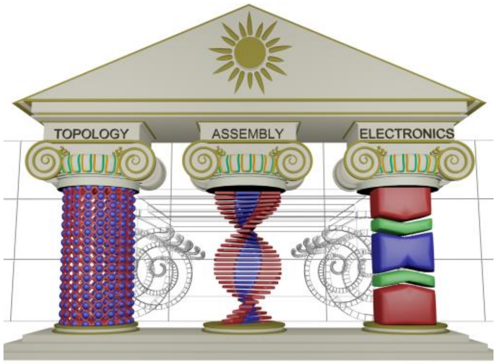


Figure 5. Photoactive supramolecular systems. (a) Porphyrin electron donors and fullerene electron acceptors assemble as a result of cooperative H-bonding and van der Waals interactions, resulting in a complex that achieves a photoinduced charge separated state. (b) Dibenzotetrathienecoronenes (DBTCCs) envelop the much larger C_{60} crystals to bring about a binary donor-acceptor motif capable of electron transfer.[89,90] The supramolecular structure comes about as a result of sulfur-sulfur interactions and the molecular conformations of the DBTCC molecules. (c) An oligophenylene vinylene-PDI donor-acceptor system that assembles into helical superstructures as a result of orthogonal π···π stacking, H-bonding interactions, and chiral side-chains appended to the donor. Charge separation is observed upon irradiation.[59,89] (d) A DPP-PDI donor-acceptor supramolecular polymer that forms helical supramolecular polymers as a result of cooperative H-bonding and π···π stacking, and undergoes photoinduced charge separation in solution and in the solid-state.[35] (e) Donor-bridge-acceptor composed of PDI donors and DPP acceptors that stacks in the solid-state, resulting in a long-lived charge separated state following irradiation.[92]

Abstract Picture.



Supramolecular polymers for solar energy harvesting can be created by considering carefully the relationship between topology, assembly, and photophysics.