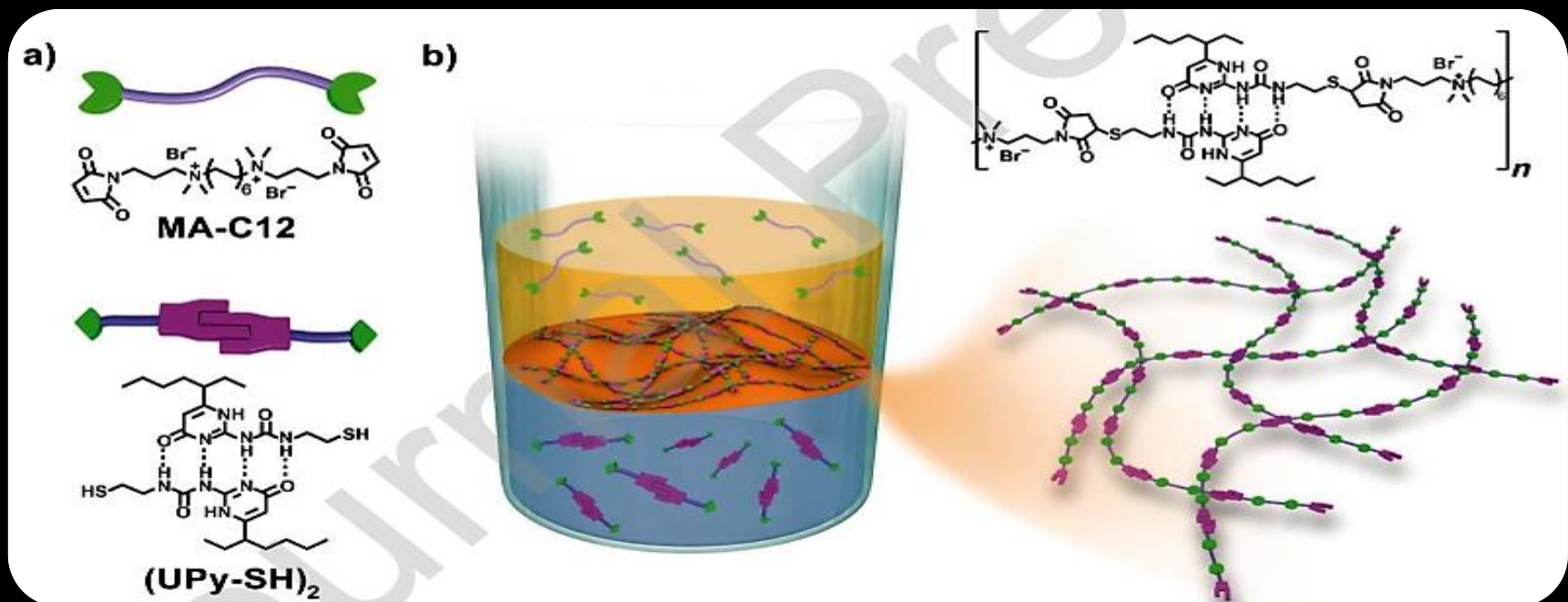


1. Supramolecular polymers

Supramolecular polymers, as a representative of supramolecular polymeric systems based on small molecules, are defined as polymeric arrays of monomeric units that are held together by highly directional and reversible noncovalent interactions, resulting in polymeric properties in solution and bulk

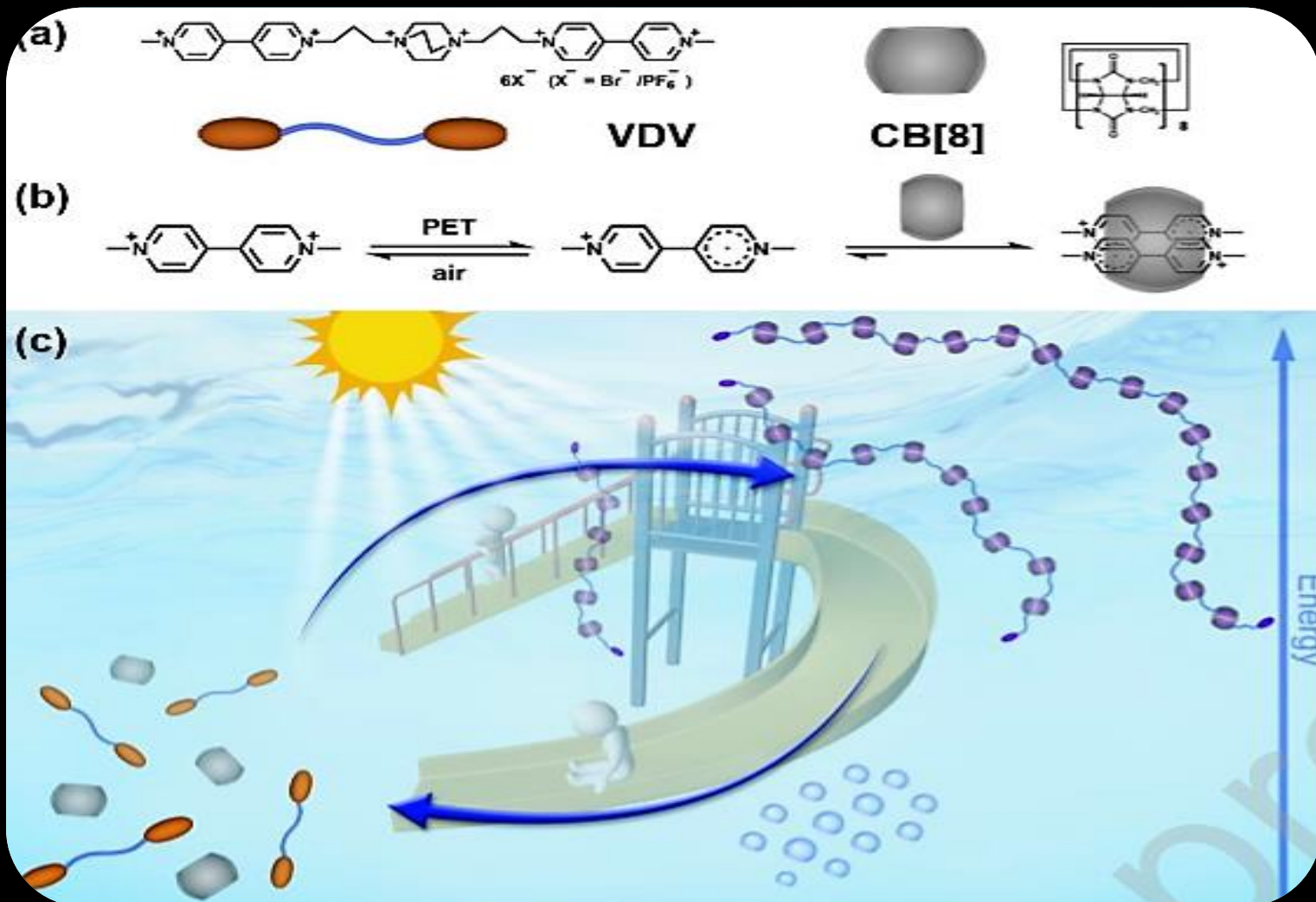
1.1. Supramolecular interfacial polymerization

- The noncovalent interactions should be strong enough to form supramonomers with well-defined structures.
- the reaction at the water-oil interface should be highly efficient under mild conditions.
- the noncovalent interactions and the covalent polymerization should be orthogonal and do not interfere with each other.



(a) Chemical structures of the water-soluble monomer MA-C12 and oil-soluble supramonomer (UPy-SH)₂;
(b) a schematic diagram of supramolecular interfacial polymerization at the water-oil interface

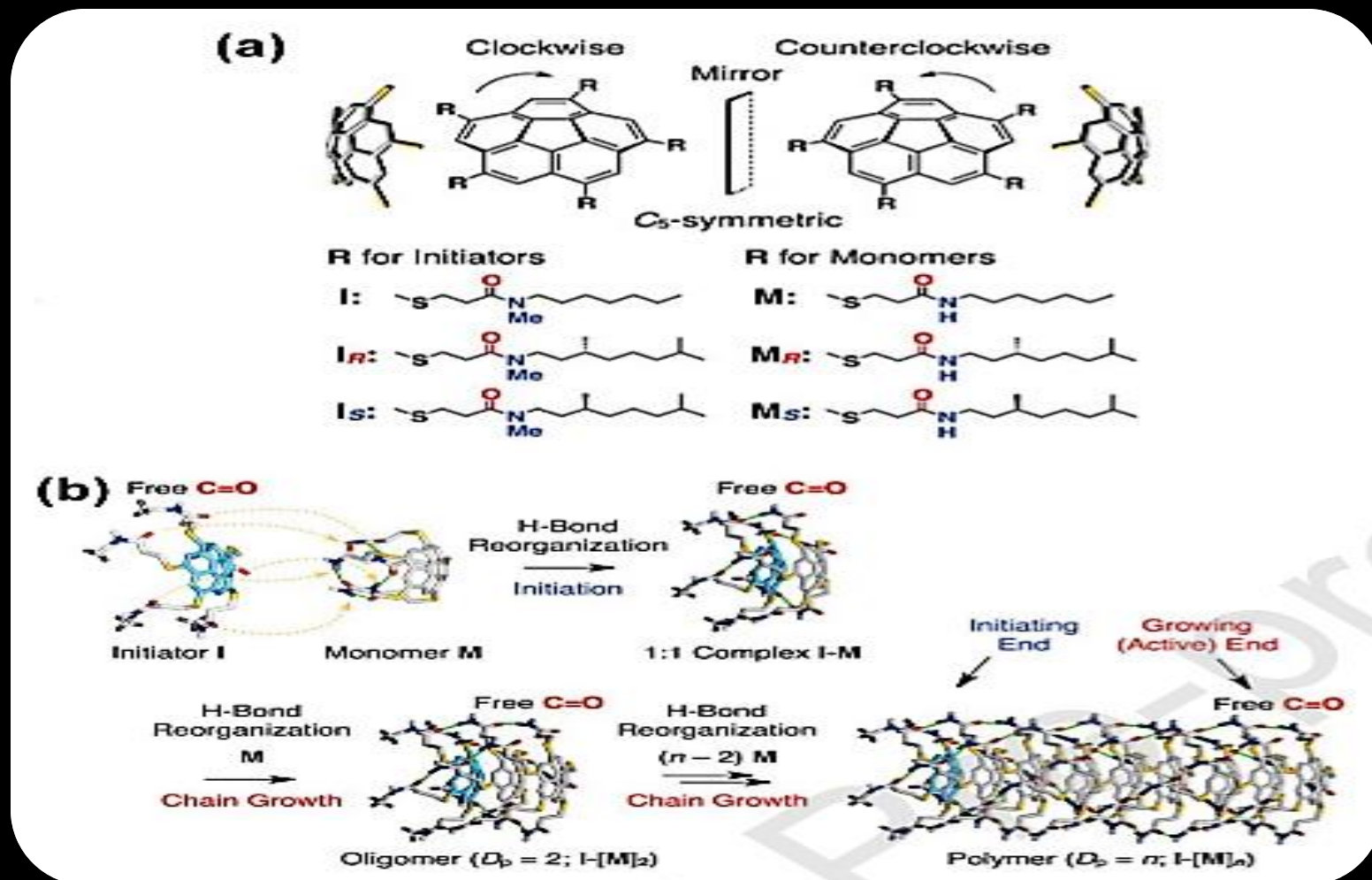
1.2. Dissipative supramolecular polymerization



(a) Chemical structures of monomer VDV and CB[8]. (b) Redox reaction of viologen and host-guest complexation of viologen cation radical and CB[8]. (c) Schematic diagram of dissipative supramolecular polymerization powered by light. Upon inputting energy by light, the system was driven "upstairs" to far-from equilibrium states, and supramolecular polymerization was implemented. In addition, the system returned to equilibrium spontaneously by air oxidation, and supramolecular polymers depolymerized

1.3. Living supramolecular polymerization

more metastable monomers could also be implemented to prepare supramolecular polymers with controlled molecular weights through living chain-growth supramolecular polymerization.



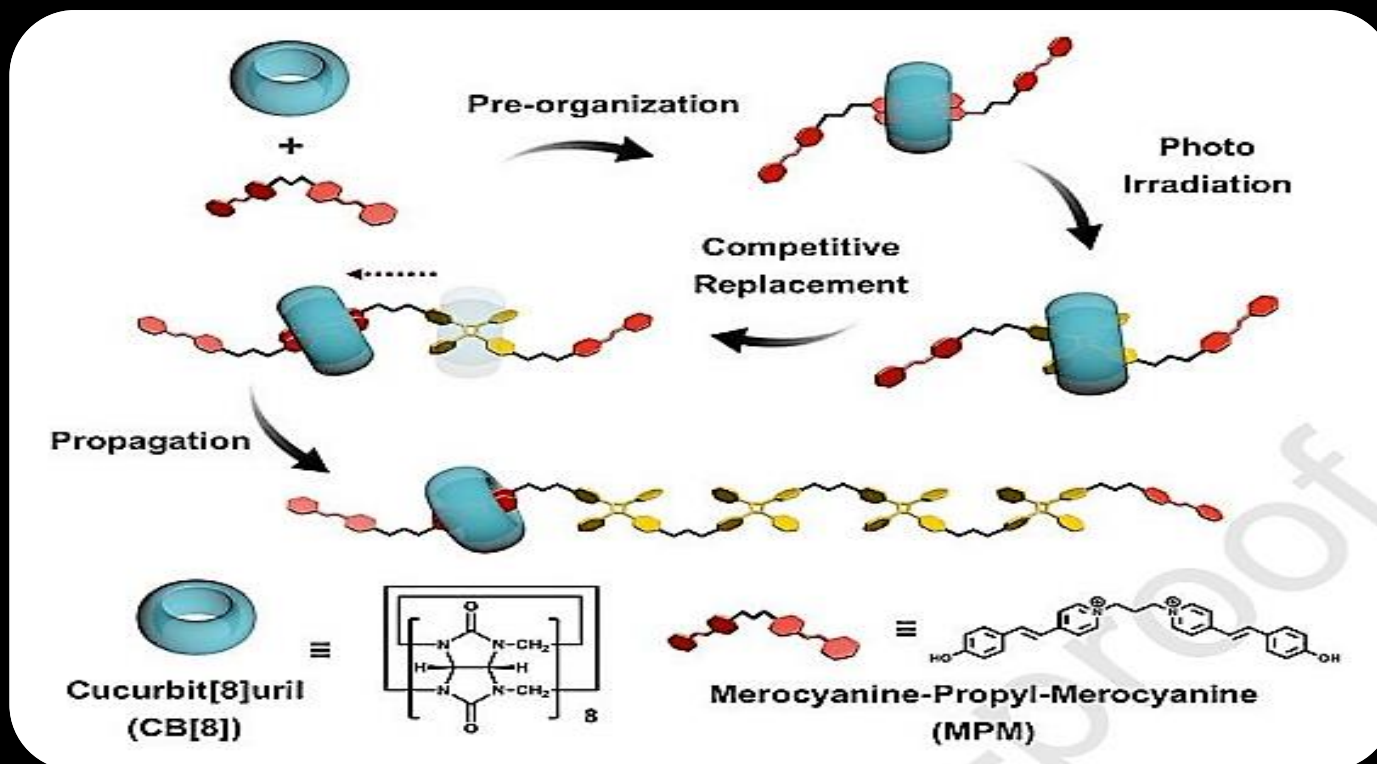
(a) Chemical structures of monomers and initiators; (b) schematic representation of the chain-growth supramolecular polymerization of monomers initiated with designed initiators

2. Supramolecular polymeric systems based on small molecules and polymers

The noncovalent interactions between small molecules and polymers have been successfully utilized to regulate the process of polymerization and prepare polymers with controlled structures

2.1 Supramolecular catalyzed polymerization based on macrocycles

macrocyclic host molecules were used as supramolecular catalysts to accelerate the reactions in the solution through the host-guest interaction by encapsulating the substrates into the confined spaces of the macrocyclic host molecules



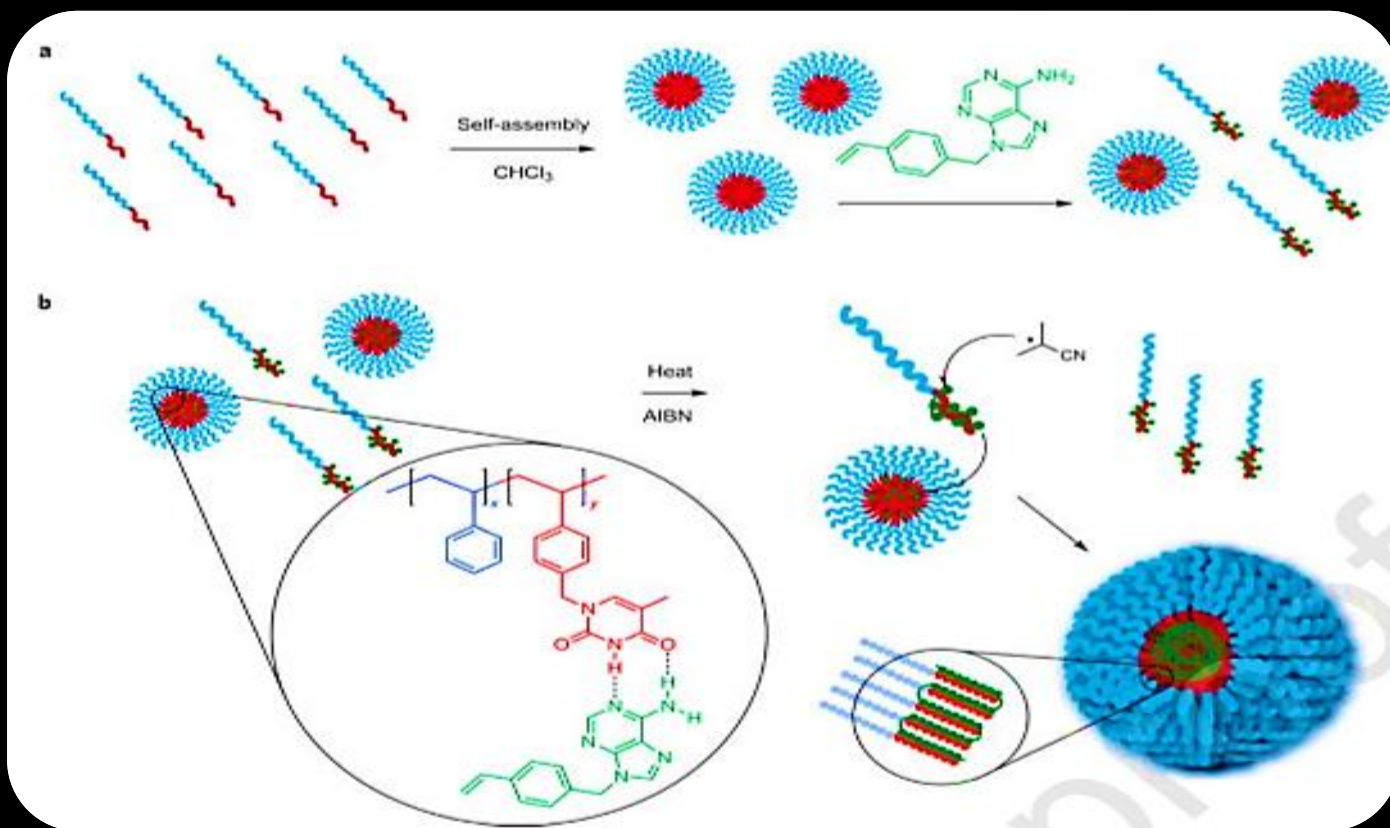
Schematic illustration of supramolecular catalyzed polymerization based on cucurbit[8]uril

2.2 Supramolecular segregation/templating polymerization

Inspired by biological templating mechanisms, nucleobase-containing synthetic polymers have been utilized to construct DNA analogues through complementary hydrogen bonds between templates and monomers



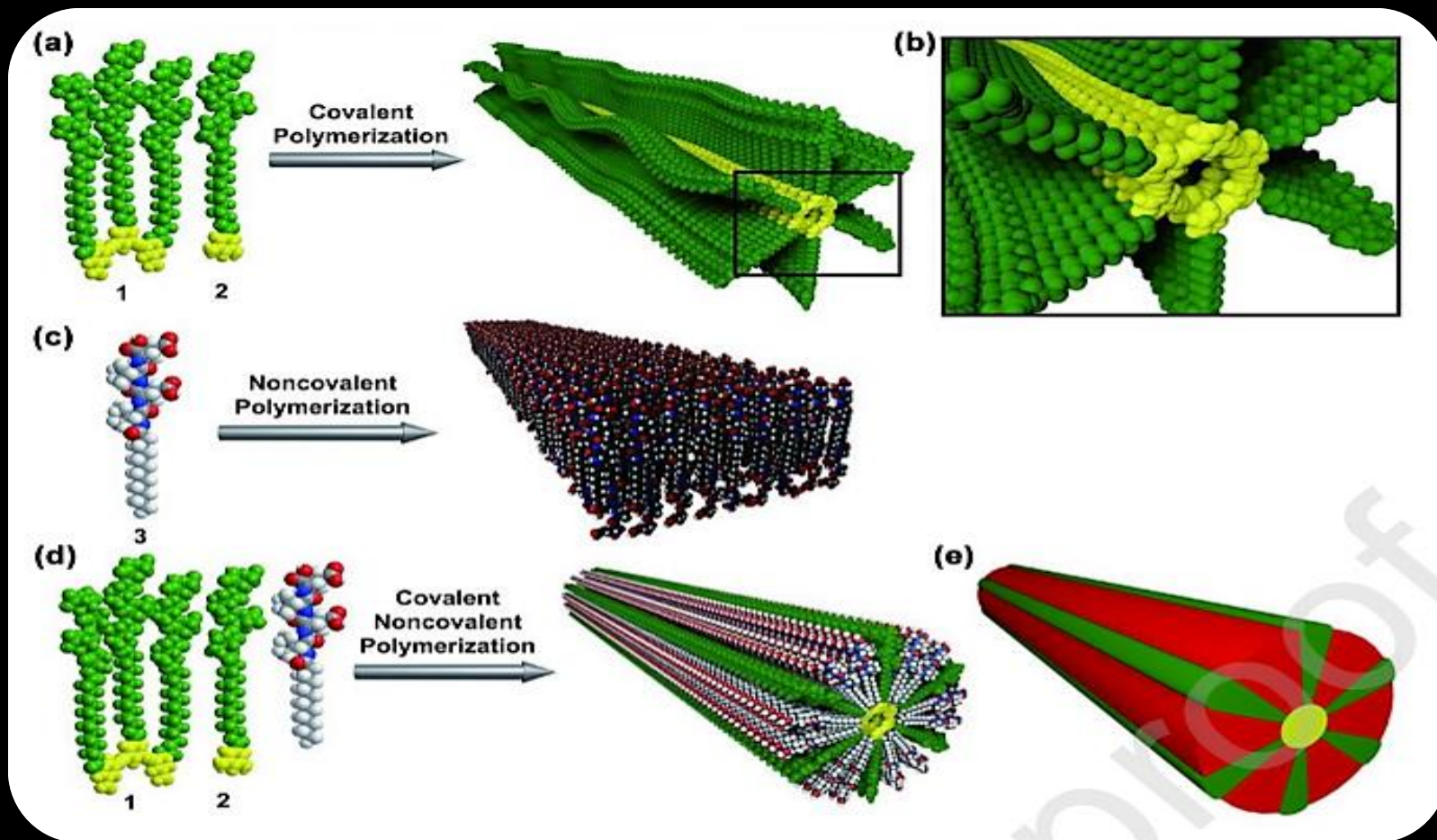
The templating polymers in homogeneous solution are not segregated, which cannot prevent propagating radicals reacting with other propagating species and monomers.



(a) Self-assembly of template block copolymer PS-b-PVBT in CHCl_3 and the dynamic exchange of monomer-loaded template after adding the complementary adenine monomer (VBA); (b) the formation of high Mw and low PDI daughter polymer (PVBA) in the micelles after the addition of AIBN and heating

2.3 Simultaneous covalent and noncovalent hybrid polymerizations

If the covalent and noncovalent polymerization are simultaneously manipulated in a hybrid system, covalent and supramolecular hybrid polymers can be obtained and these multi-programmable assemblies with high complexity will enrich the library of hybrid systems for further extensive applications



Schematic representations of (a) the covalent polymerization of monomers 1 and 2 [a magnified representation (b)], (c) the supramolecular polymerization of monomer 3, and (d) the simultaneous covalent and supramolecular polymerizations to form the hybrid polymer. Illustration (d) of the hybrid polymer consisting of two distinct covalent (green and yellow) and supramolecular (red) polymers

3. Supramolecular polymeric systems based on polymers

3.1 From ordered assemblies to highly complex ordered structures

3.1.1 Crystallization-driven living self-assembly

- **Crystallization-driven living self-assembly was discovered by Winnik, Manners and coworkers**
- **block copolymers containing both crystalline, organometallic coreforming polyferrocenylsilane (PFS) and polyisoprene (PI) blocks could form cylindrical micelles**
- **the length of these cylindrical micelles was precisely controlled**

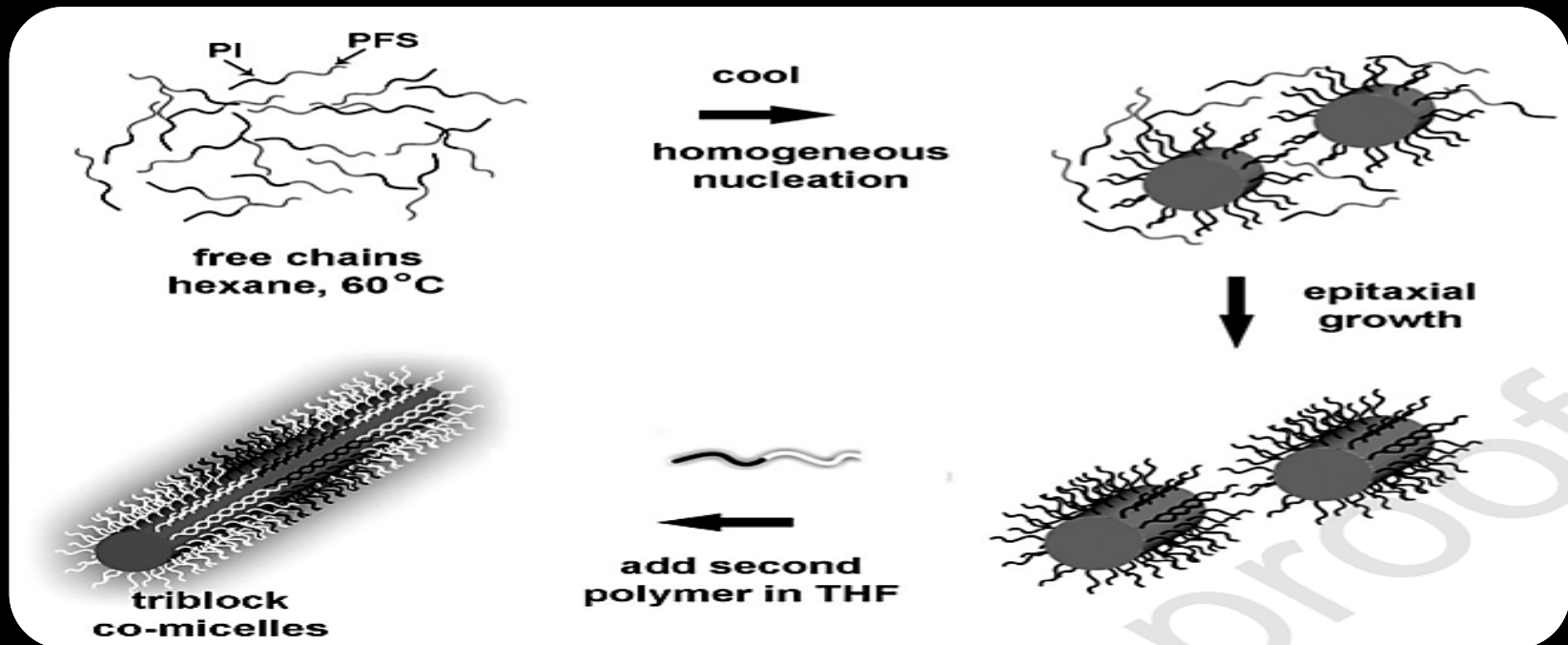


Illustration of the mechanism for the crystalline-driven living self-assembly of PFS-PI block copolymers. Cylindrical micelles with a relatively narrow distribution of lengths can be formed after the homogeneous nucleation and epitaxial growth. The ends of cylindrical micelles remain active to further growth after adding another polymer containing the same PFS core

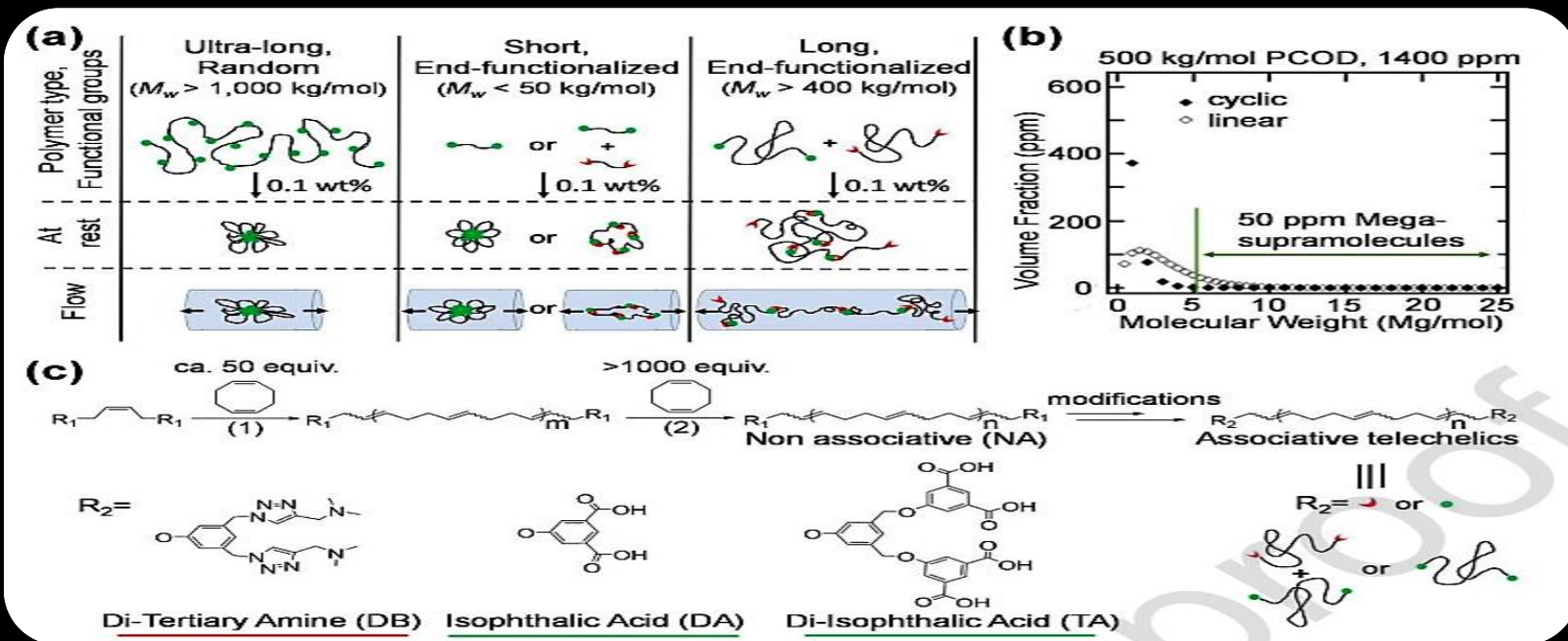
3.2 Functional supramolecular materials

Supramolecular polymeric systems containing polymeric building blocks may exhibit good mechanical performance owing to the entanglement of polymer chains and hold great potentials for constructing functional materials

3.2.1 Megasupramolecules as jet fuel stabilizer

Ultralong polymers are used to control the mist and reduce the drag in flow, and the fuel can form larger droplets under the impact in this case

Ultralong covalent polymers usually are in the entangled state due to the high molecular weights of such polymers, thus blocking the fuel pumps.

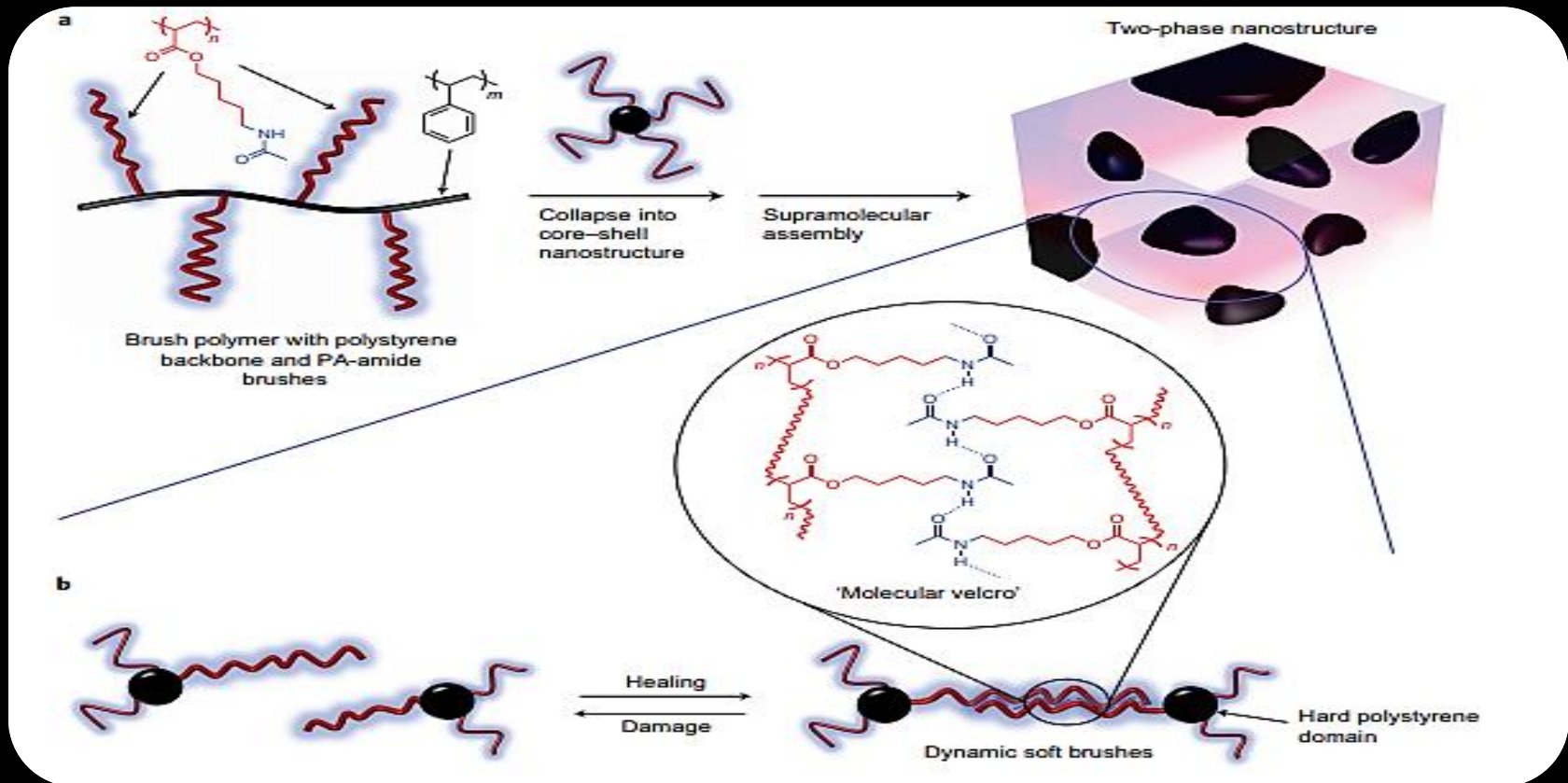


(a) Proposed assembly of randomly functionalized associative ultra-long polymers (left), short telechelic polymers (center), and long telechelic polymers (right) at rest and in flow; (b) ring-chain equilibrium distribution of cyclic and linear species; (c) synthetic routes of long telechelic polymers with different associative groups

3.2.2 Advanced self-healing supramolecular materials

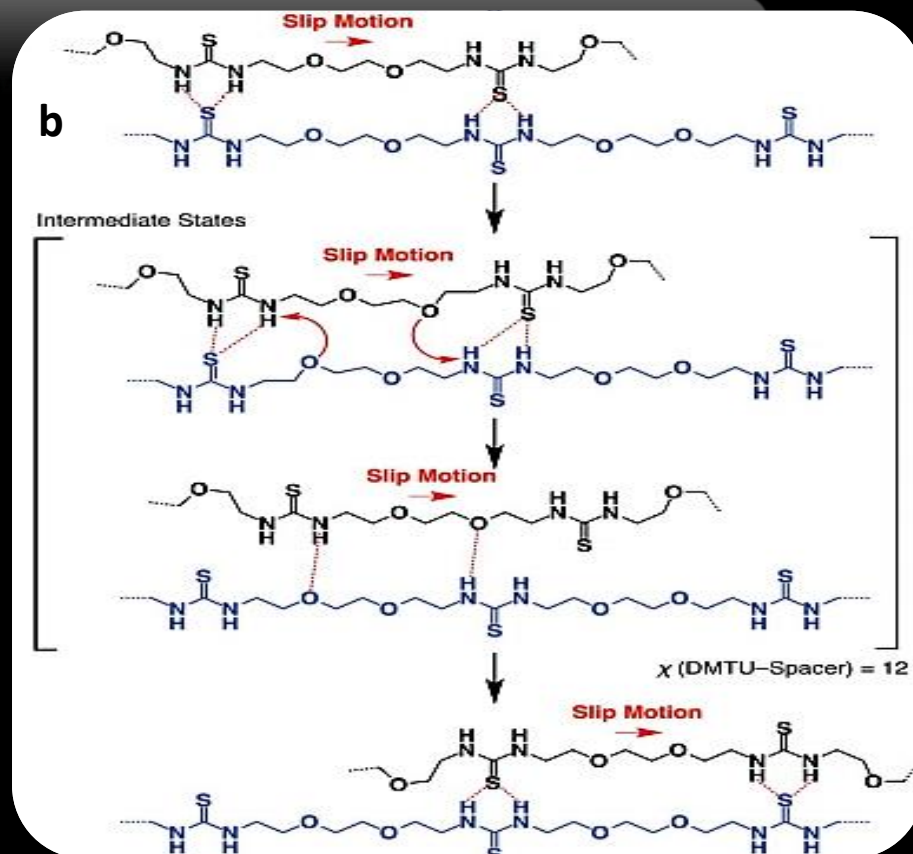
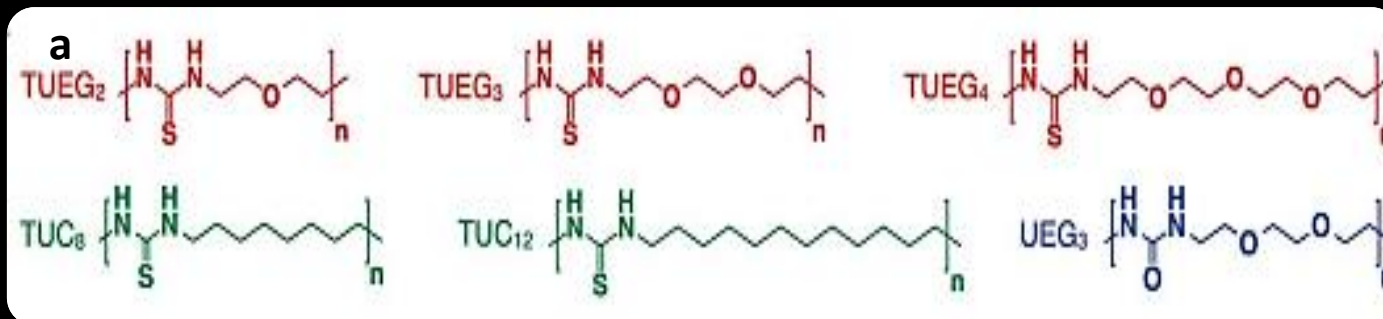
3.2.2.1 Multiphase self-healing supramolecular polymeric systems

- ❑ Most self-healing materials rely on either the input of external energy or adding the healable agents including monomers, solvents or plasticizers
- ❑ Such materials are always subject to the trade-off between the healing efficiency and mechanical properties owing to the restricted mobility in rigid systems



(a) Schematic representation of the hydrogen-bonding brush polymer self-assembly process into two phase nanostructures. (b) Illustration of reversible rupture of supramolecular connections under stress and healing process owing to the dynamic nature of hydrogen-bonding interactions between soft brush polymers

3.2.2.2 Self-healing supramolecular polymeric glass



- ❖ The mechanism of self-healing properties was proposed that ethylene glycol spacers could regulate the activation energy for the exchange of hydrogen-bonded thiourea pairs via slip motion
- ❖ These robust yet healable polymers cross-linked by hydrogen bonds suggest that the selfhealing property is also possible even though the mobility of polymer chains is fully limited in this supramolecular polymeric system

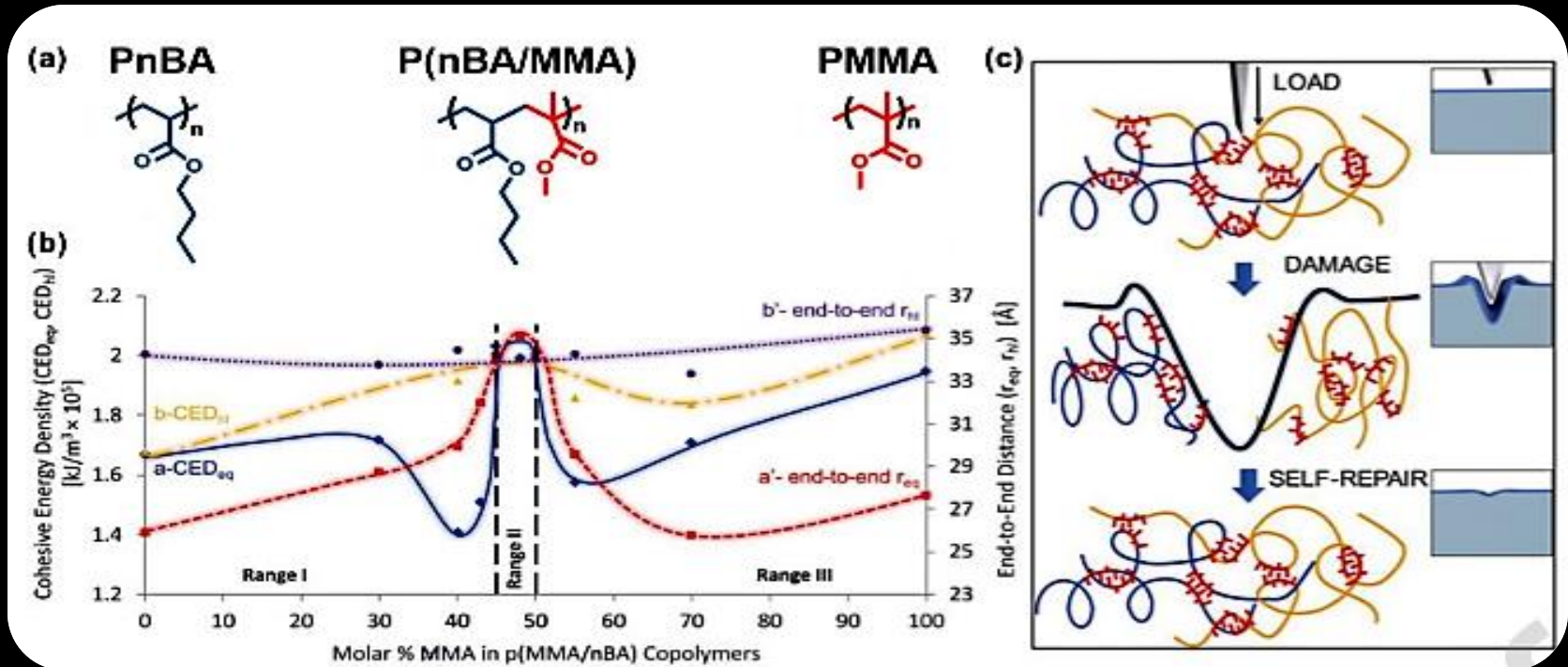
(a) Chemical structures of poly(ether-thioureas) with different ethylene glycol units (TUEG_n, n = 2, 3, 4) and different alkyl chains (TUC_n, n = 8, 12) and poly(ether-urea) with triethylene glycol units (UEG₃); (b) proposed self-healing mechanism of how the exchange of hydrogen-bonded thiourea pairs in poly(ether-thiourea) chains (TUEG₃)

3.2.2.3 Key-and-lock commodity self-healing copolymers

Through incorporating dynamic covalent bonds or noncovalent interactions within the chains, polymers are capable of intrinsic self-healing under mechanical damage owing to the exchange and reforming of the reversible bonds

However, in these systems, the modification of dynamic building blocks typically requires elaborate synthetic steps or the design of polymers which are considerably distinct in cost and chemical composition from commercial materials

Urban and colleagues reported a set of commercially available copolymers which could autonomously repair simply through the weak van der Waals (vdW) interactions within the polymer chains

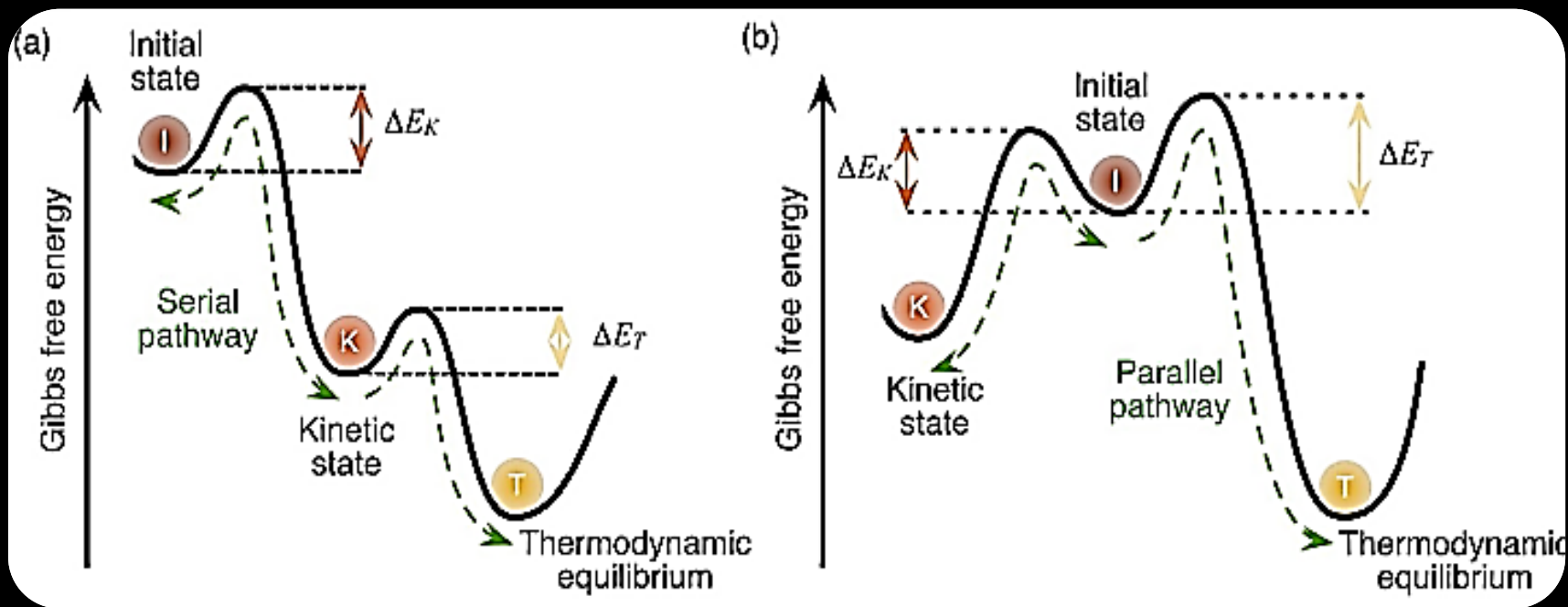


(a) Chemical structures of poly(n-butyl acrylate) (PnBA), poly(methyl methacrylate) (PMMA) and poly(n-butyl acrylate)/(methyl methacrylate) [P(nBA/MMA)] copolymers; (b) cohesive energy densities at equilibrium (CED_{eq}) (curve a) and for forced helical conformations (CED_{hl}) (curve b), end-to-end chain distances at equilibrium (r_{eq}) (curve a') and for forced helical conformations (r_{hl}) (curve b') as a function of molar ratio of MMA in the copolymers; (c) the presence of key-and-lock associations (red) through vdW interactions facilitates chain recovery under damage

2. kinetically controlled supramolecular polymerization

conventional covalent polymerization : the kinetic factors are dominant over the thermodynamic factors

supramolecular polymerization : thermodynamic factors dominate the system



Schematic illustration of the energy landscape in supramolecular polymerization. Two possible pathways, serial pathway (a) and parallel pathway (b), when a monomer undergoes supramolecular polymerization from the initial state (I) to a kinetically (K) and/or a thermodynamically stable state (T). E_K and E_T represent activation energies for the kinetically and thermodynamically stable states, respectively

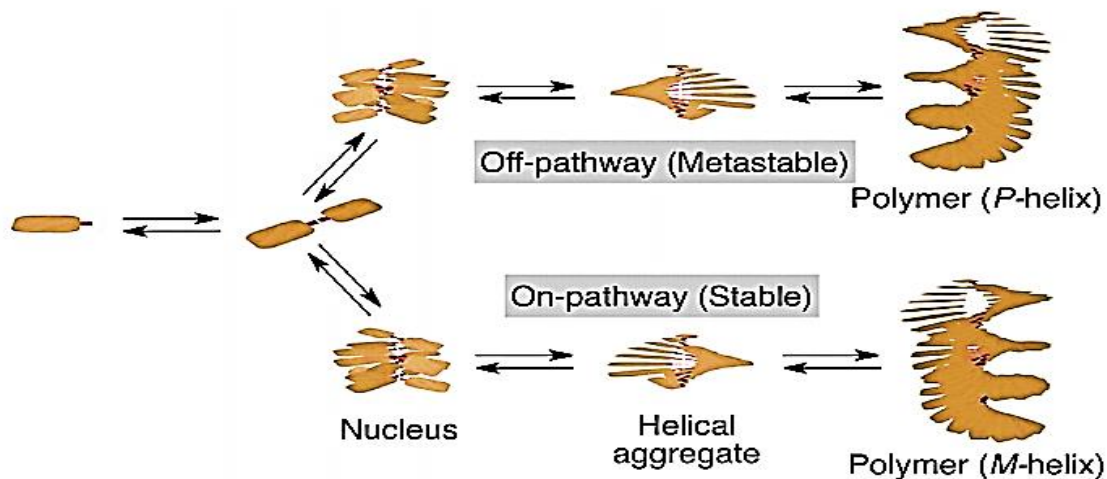
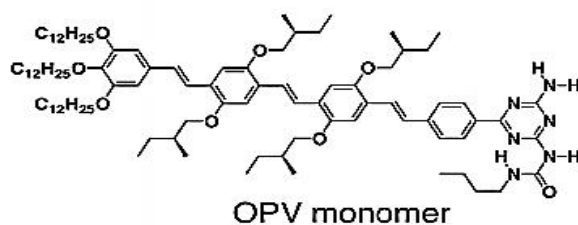
2.1. Pathway complexity in supramolecular polymerization

Pathway complexity allows one to understand the kinetic aspects of supramolecular polymerization.



supramolecular polymers of a chiral bis(merocyanine) derivative display opposite chiroptical profiles

formation of a nanorod in the former case and the formation of a random coil in the latter case was confirmed



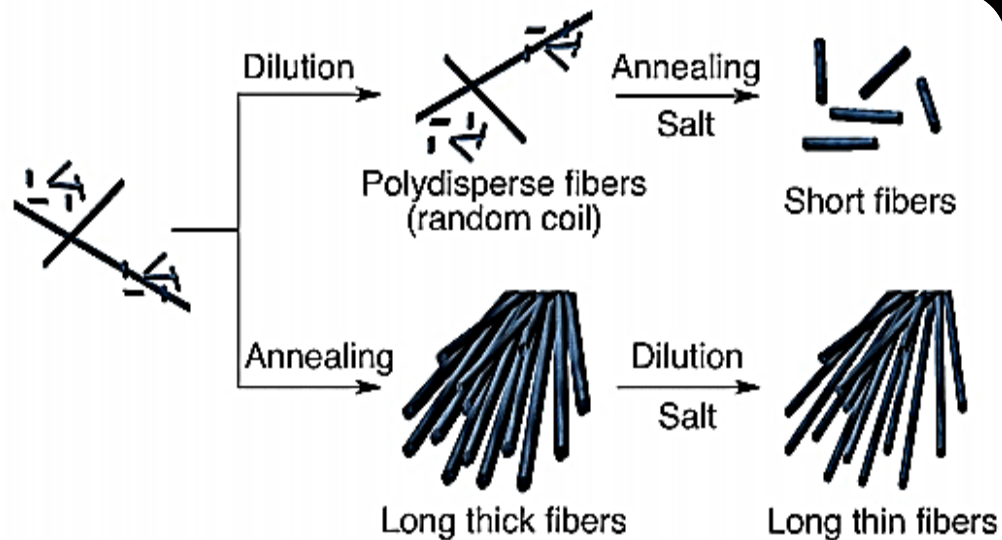
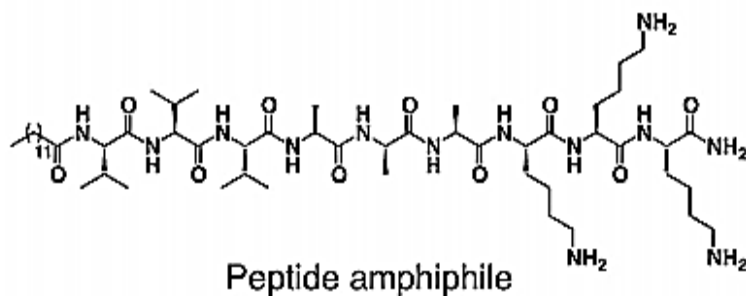
Chemical structure of an OPV monomer and schematic illustrations of the (M) and (P) helical supramolecular polymers

2001

A series of peptide amphiphiles developed that undergo supramolecular polymerization to form structurally defined nanofibers with an average diameter of 8 nm and a length of several microns

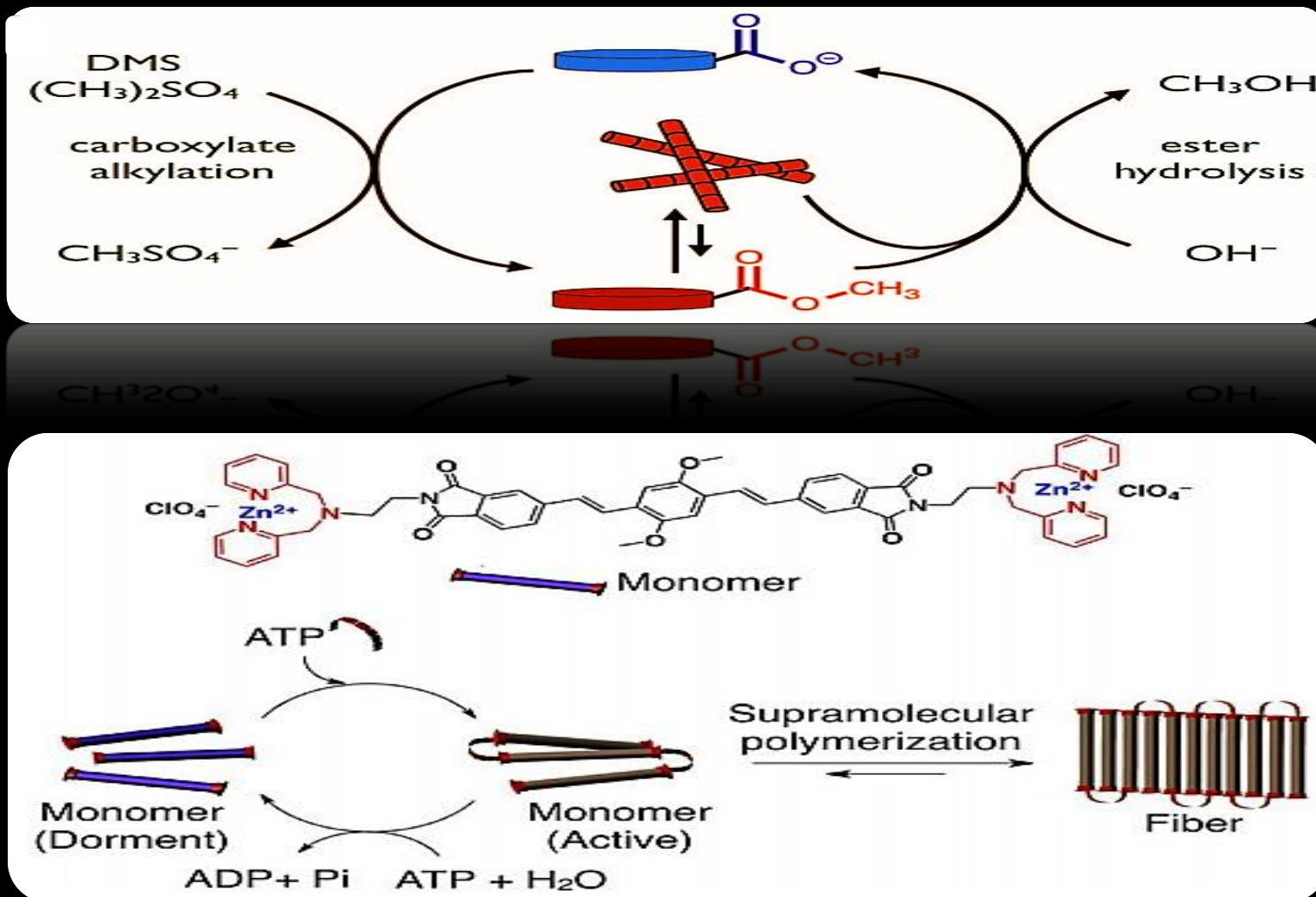
2014

A peptide amphiphile (PA) in a water/ $(\text{CF}_3)_2\text{CHOH}$ (HFIP) mixture undergoes pathway-controlled supramolecular polymerization



Chemical structure of an OPV monomer and schematic illustrations of the short and long fibers of an amphiphilic peptide monomer obtained by different pathways in supramolecular polymerization

2.2. Stimuli-induced supramolecular polymerization

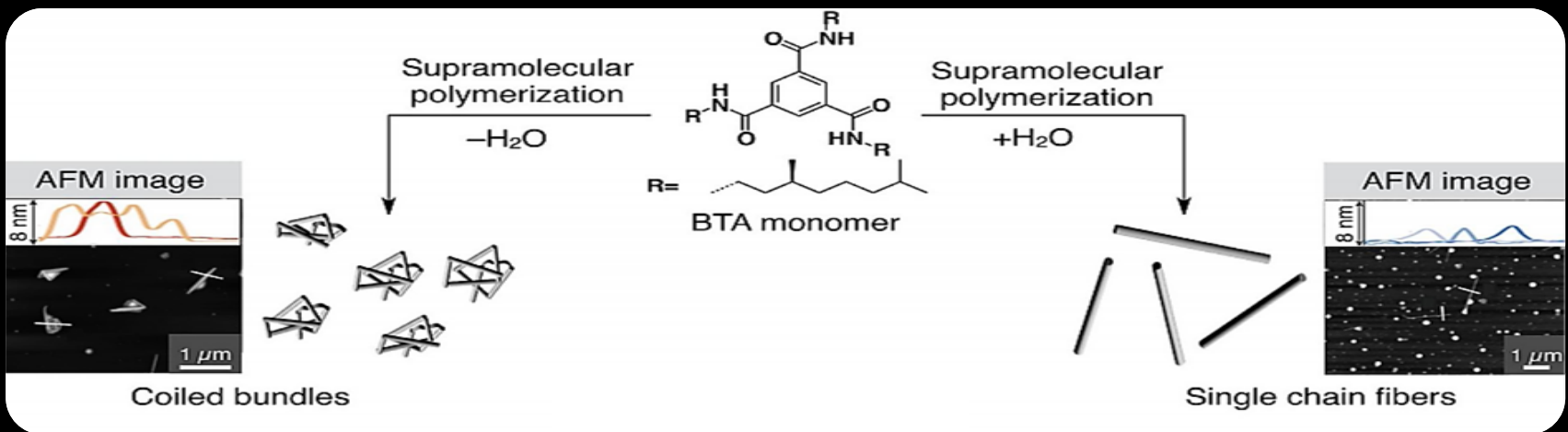
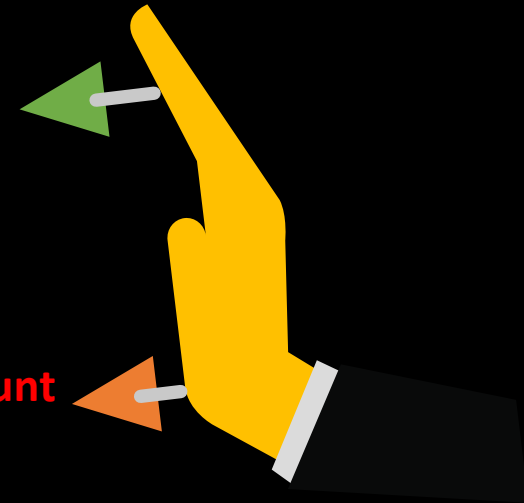


Stimuli-induced supramolecular polymerization. Chemical structure of a monomer and schematic illustration of its supramolecular polymerization in the presence of ATP stimulus.

2.3. Media effects on supramolecular polymerization

Ionic polymerization : requires dry media
The growing species are easily decomposed if the media are contaminated with water

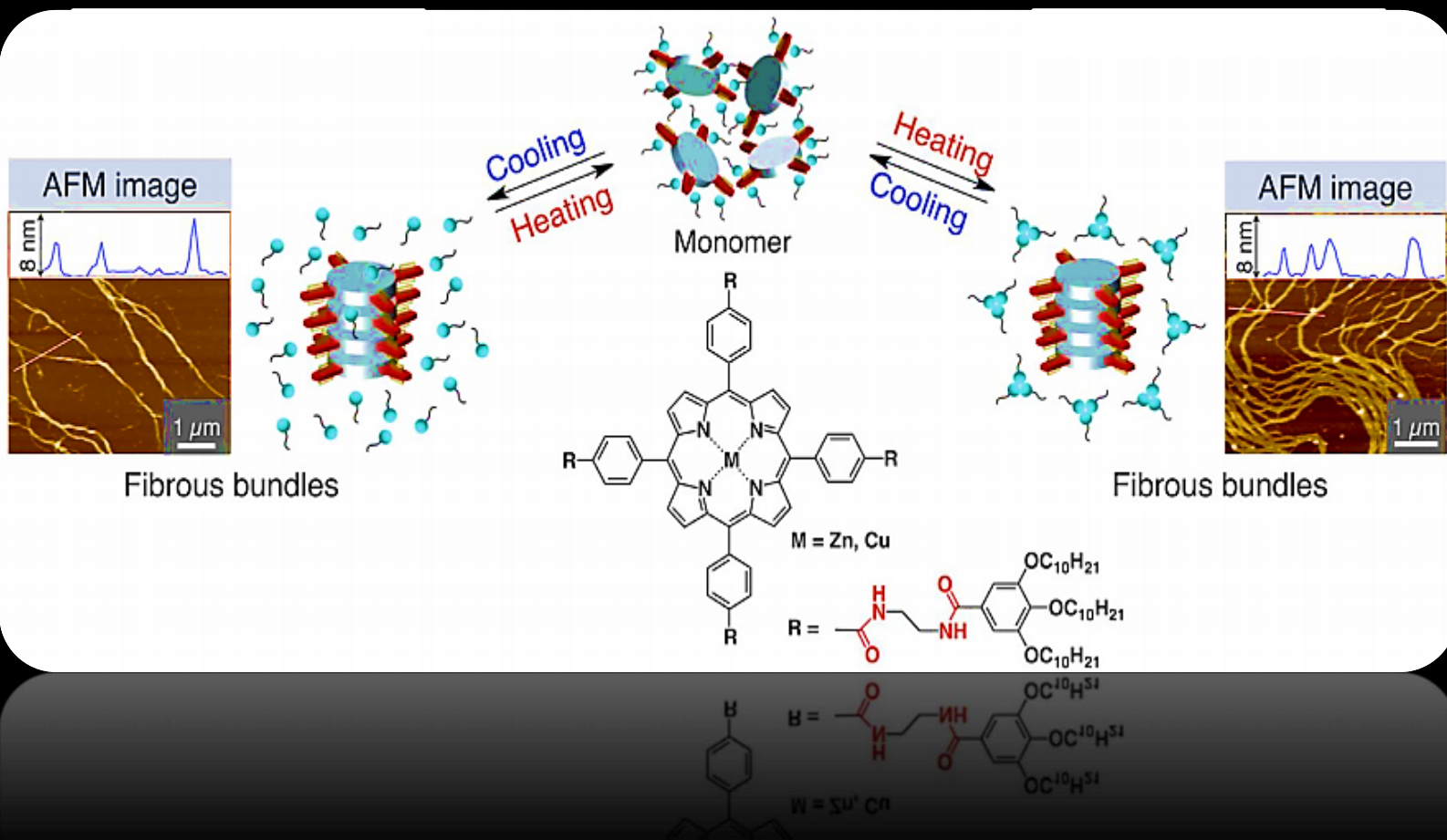
Supramolecular polymerization : reagent-grade dry hydrocarbon solvents
it has been considered to be insensitive to water if the amount of water is limited



Chemical structure of a BTA-based monomer and schematic illustration of its supramolecular polymerization in MCH in the presence or absence of water contaminant

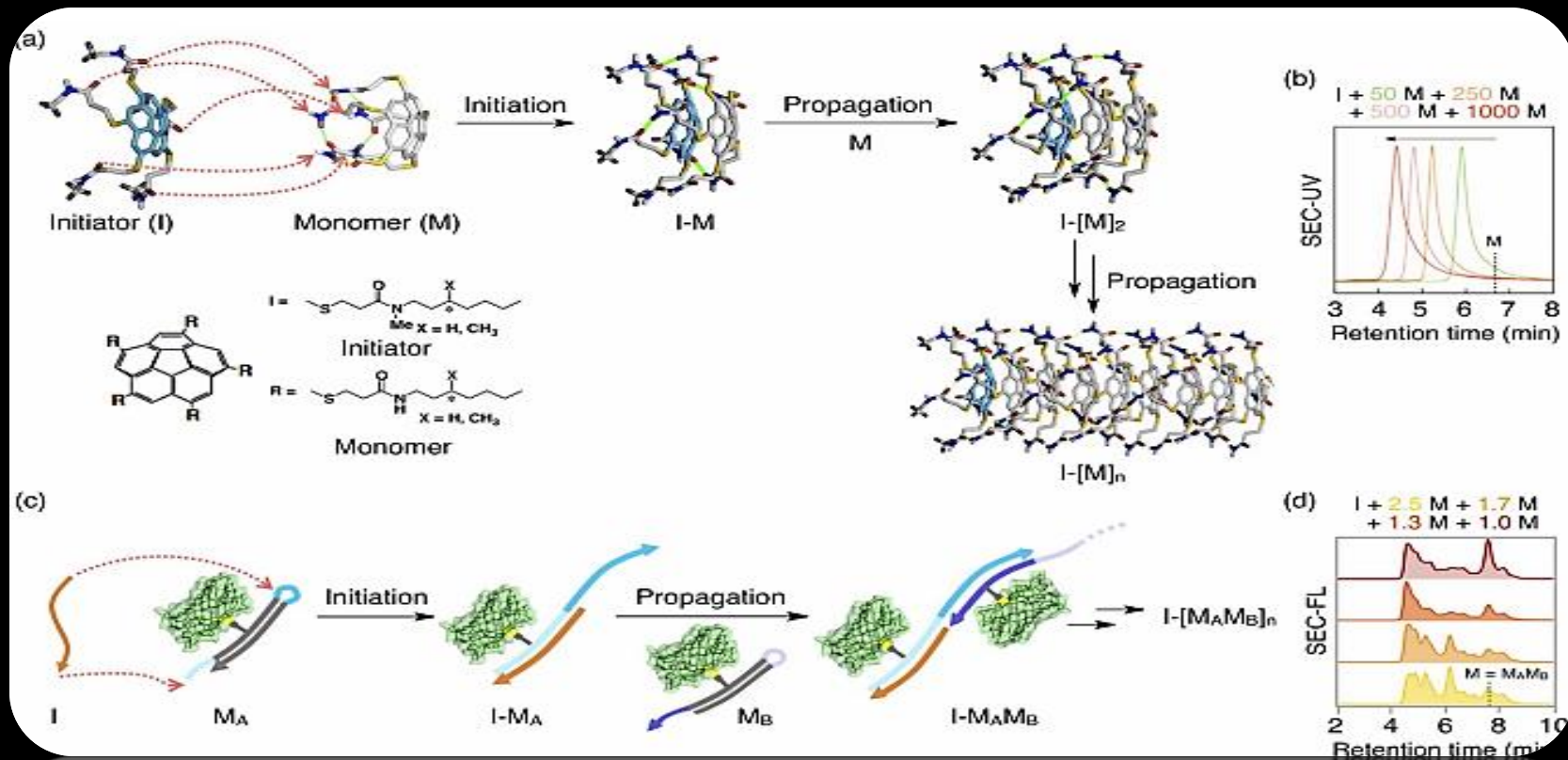
2.4. Thermally bisignate supramolecular polymerization

Conventional wisdom suggests that supramolecular polymers are more stable at lower temperatures and dissociate upon heating



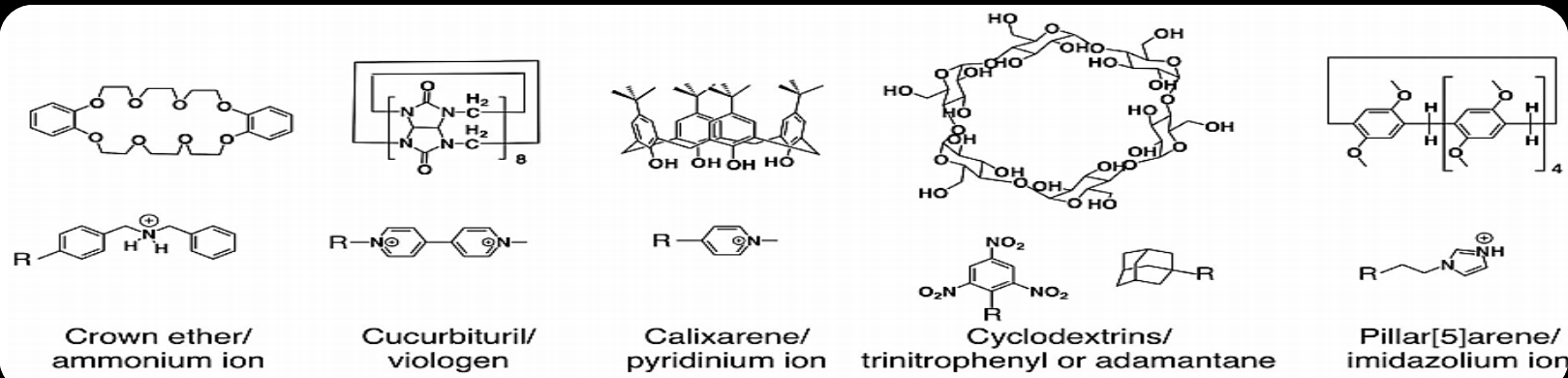
2.5. Chain-growth supramolecular polymerization

One prerequisite for realizing chain-growth supramolecular polymerizations is the design of appropriate monomers that can polymerize only by the action of initiators.

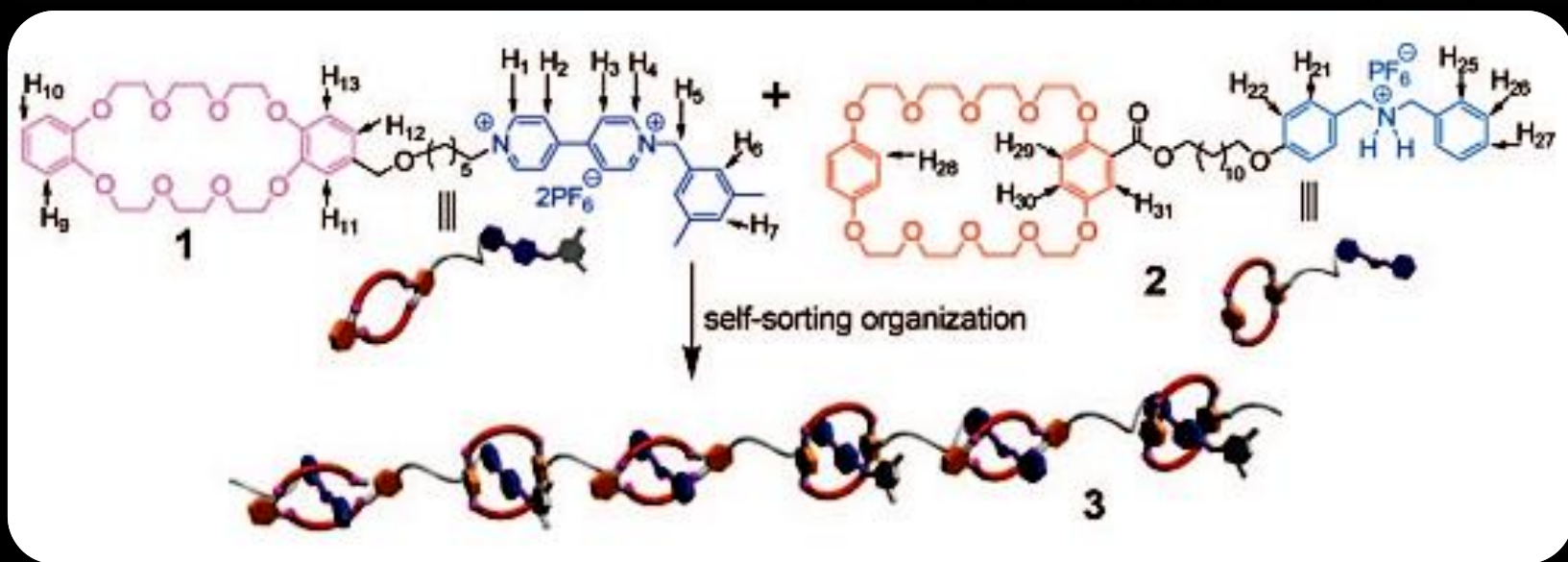


chain-growth supramolecular polymerization. Chemical structure of a corannulene-based monomer and schematic illustration of its chain-growth supramolecular polymerization using an initiator forming a 1D supramolecular polymer (a). SEC-UV traces of the supramolecular polymerization at [M]/[I] = 50, 250, 500, and 1000 (b). Schematic illustration of ring-opening supramolecular copolymerization of hairpin DNA-appended protein monomers MA and MB (MA/MB = 1/1) in the presence of a DNA strand as an initiator (I) (c). SEC-fluorescence (FL) traces of the supramolecular copolymerization at [MA + MB]/[I] = 2.5, 1.7, 1.3, and 1.0 (d)

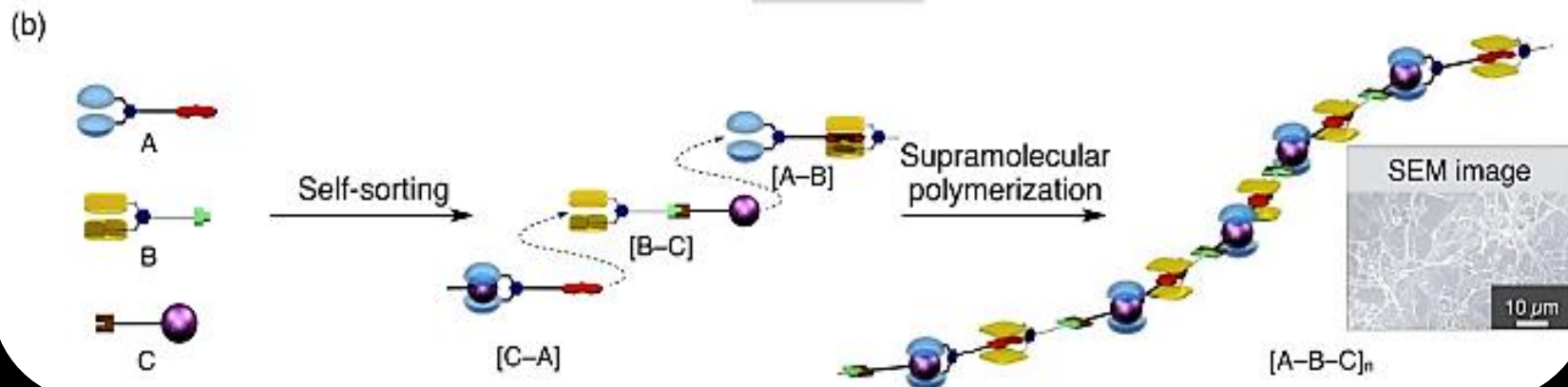
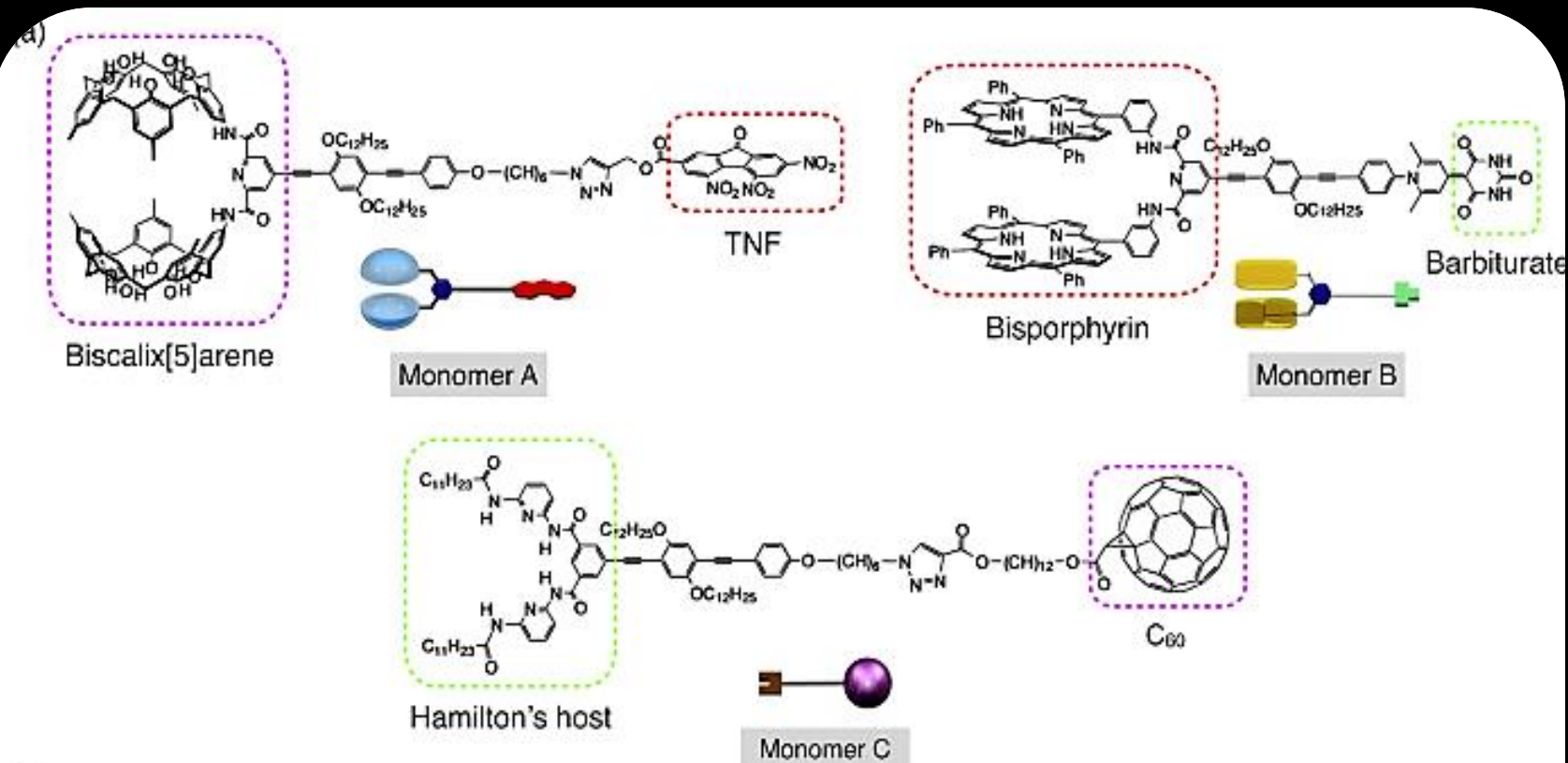
2.6. Sequence control in supramolecular copolymerization



Pairs of complimentary binding motifs for supramolecular polymerization



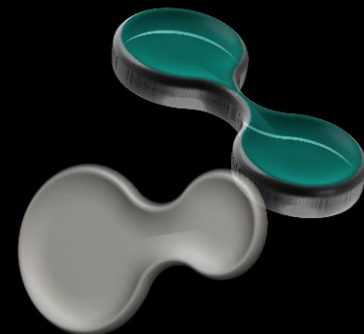
Formation of Supramolecular Alternating Copolymers 3 from Self-Sorting Organization of Heteroditopic Monomers 1 and 2



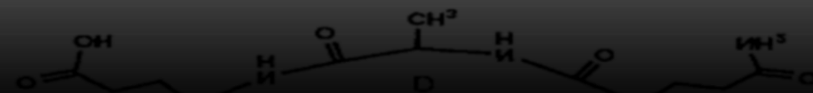
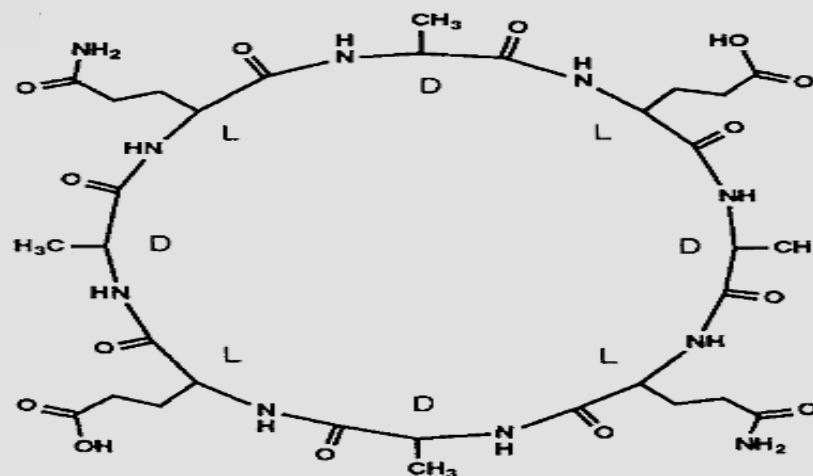
Sequence control in supramolecular copolymerization. Chemical structure and schematic illustrations of monomers A, B and C (a). Schematic illustrations of the ternary supramolecular copolymerization of A, B and C via self-sorting (b).

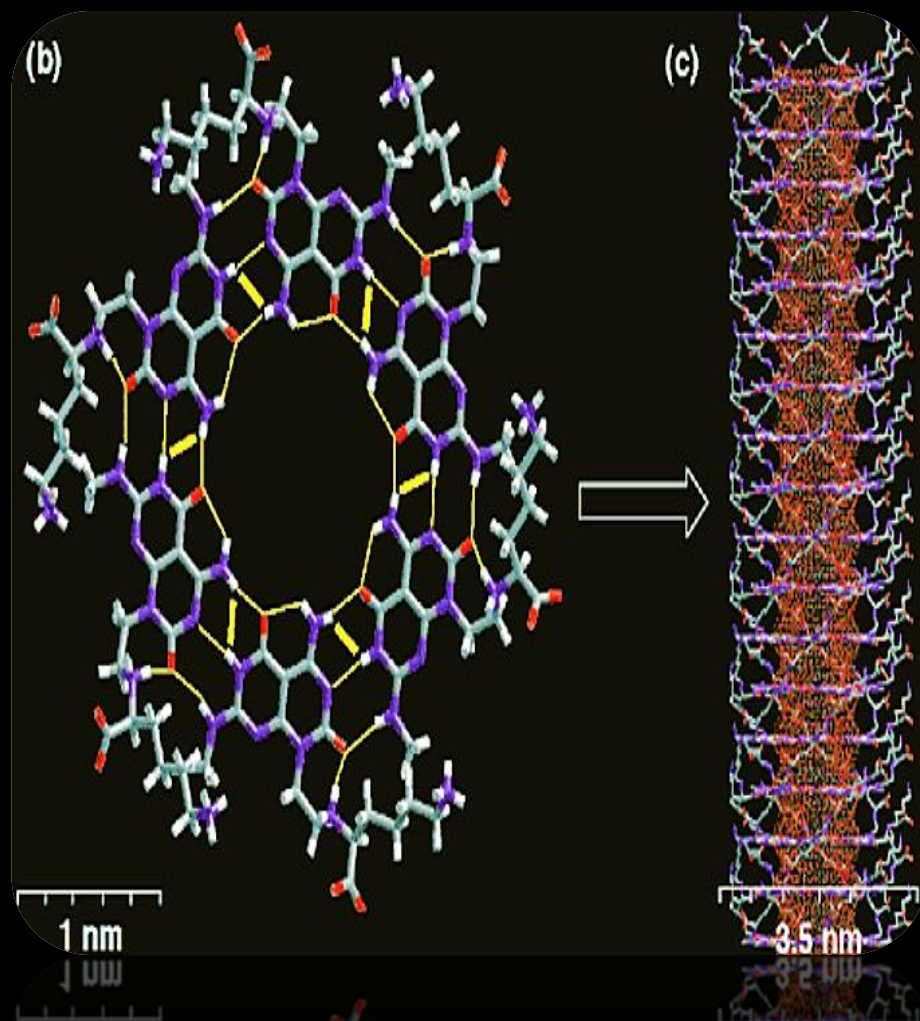
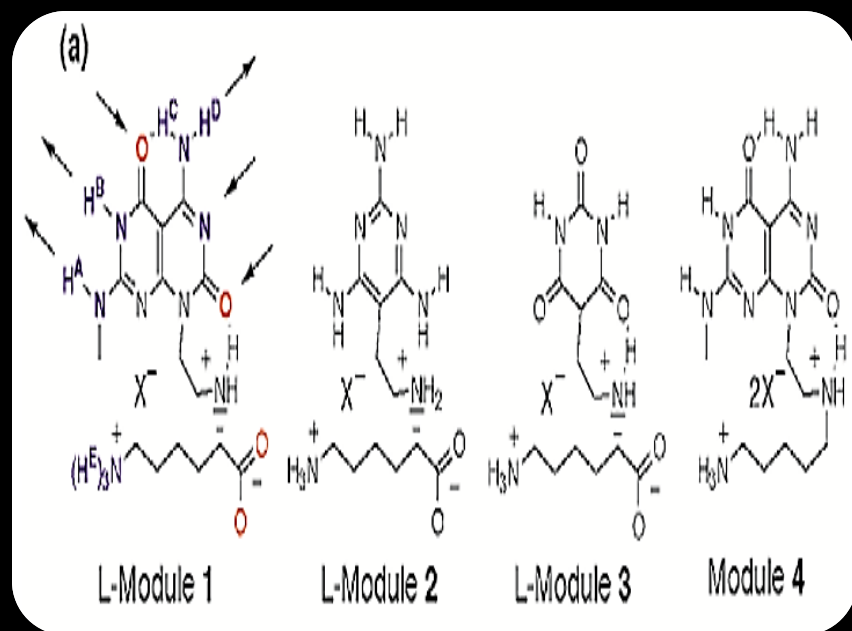
3. Nanotubular supramolecular polymerization

They are analogous to carbon nanotubes and biological nanochannels in cellular membranes, synthetic nanotubes have attracted great attention, and supramolecular polymerization is a promising synthetic methodology for their production.

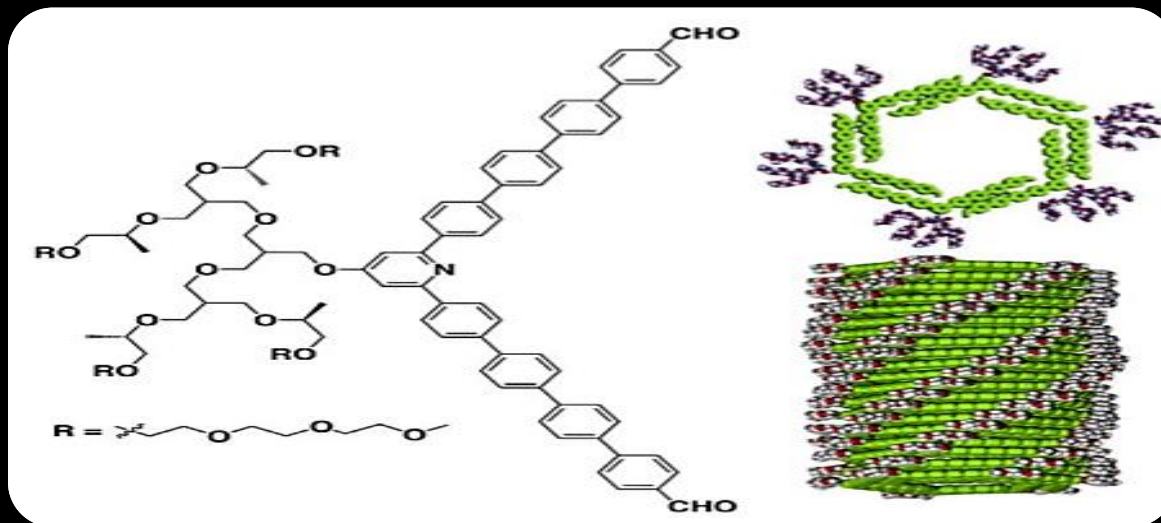


3.1. Macrocyclic monomers

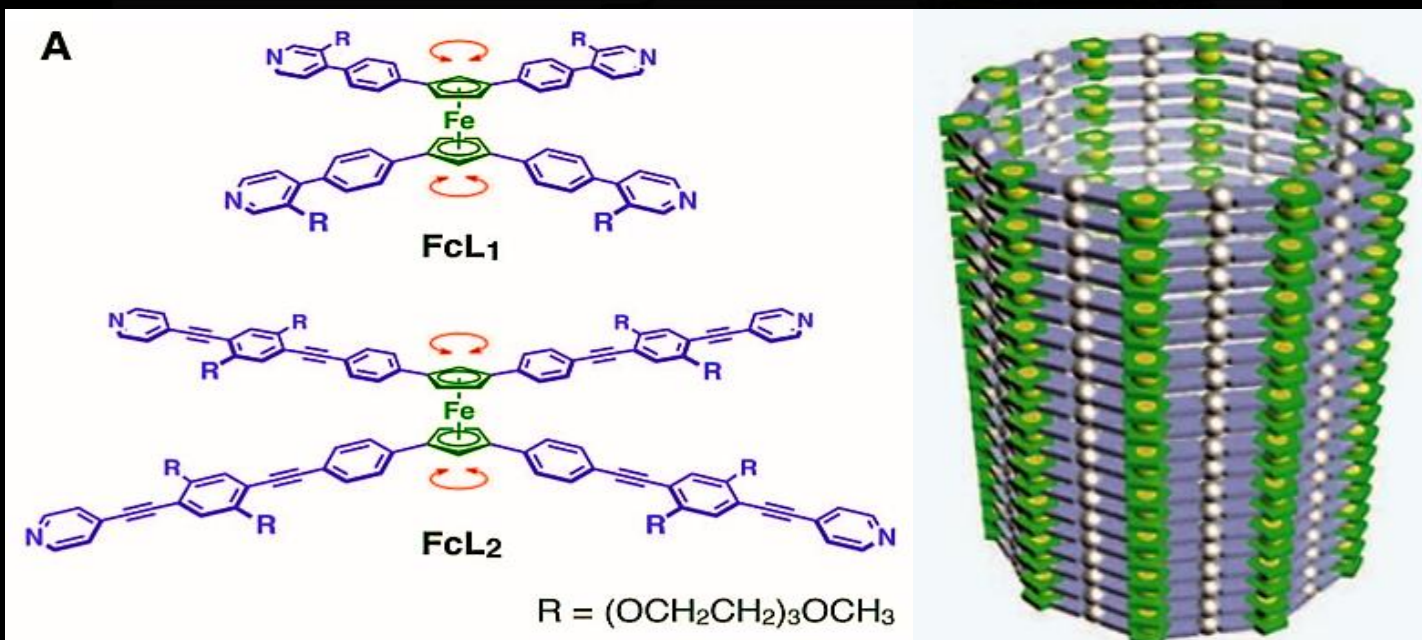




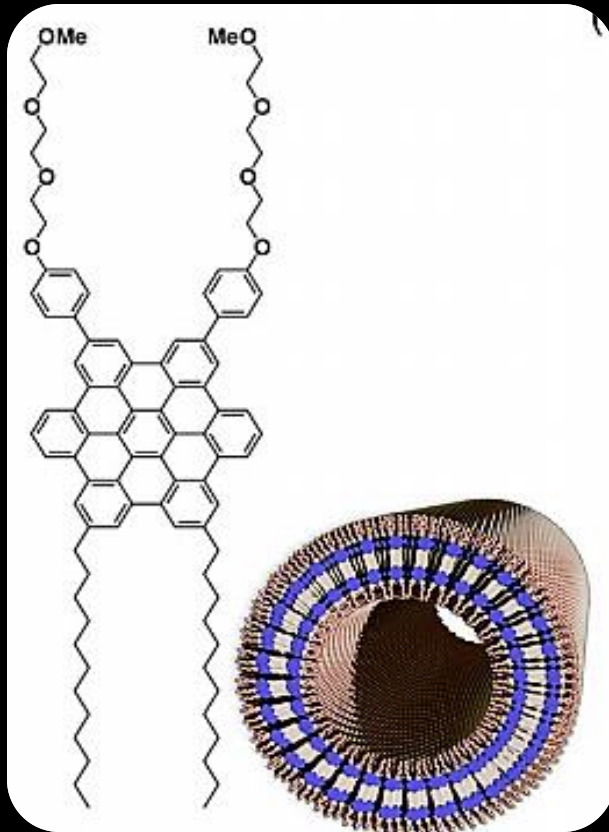
Hierarchical self-assembly of rosette nanotubes from L-module 1. (a) Modules 1-4 synthesized and investigated. (b) Molecular model of the rosette structure resulting from 1. The thin yellow lines show the hydrogen-bond network. The thick yellow lines highlight unique intermodular NOEs recorded. (c) Molecular model of the proposed nanotube. Eighteen rosettes were arranged in a tubular fashion with a starting interplane distance of 4.5 Å and 30° rotation along the tube's main axis. The inner solvent-accessible surface area of the tube is highlighted in red.



Schematic illustrations of representative nanotubular supramolecular Polymers consisting of a noncovalent macrocycle



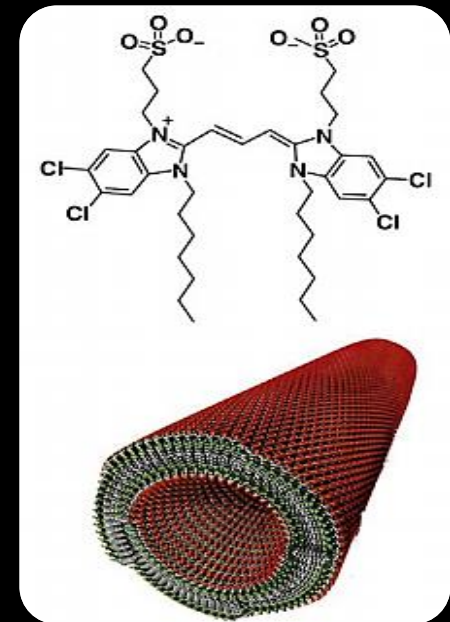
3.2. Amphiphilic monomers



HBC amphiphiles in polar solvents solvophobically assemble into a 3-nm thick 2D bilayer membrane, which rolls up into a helical tape or a nanotubular polymer

Schematic illustrations of representative nanotubular supramolecular polymers consisting of a hexa-peri-hexabenzocoronene (HBC)

In this case, a nanotubular assembly with a diameter of 20 nm forms in dry THF, whereas a helical nanocoil preferentially forms in wet THF (20% v/v water)



Schematic illustrations of representative nanotubular supramolecular polymers consisting of a cyanine

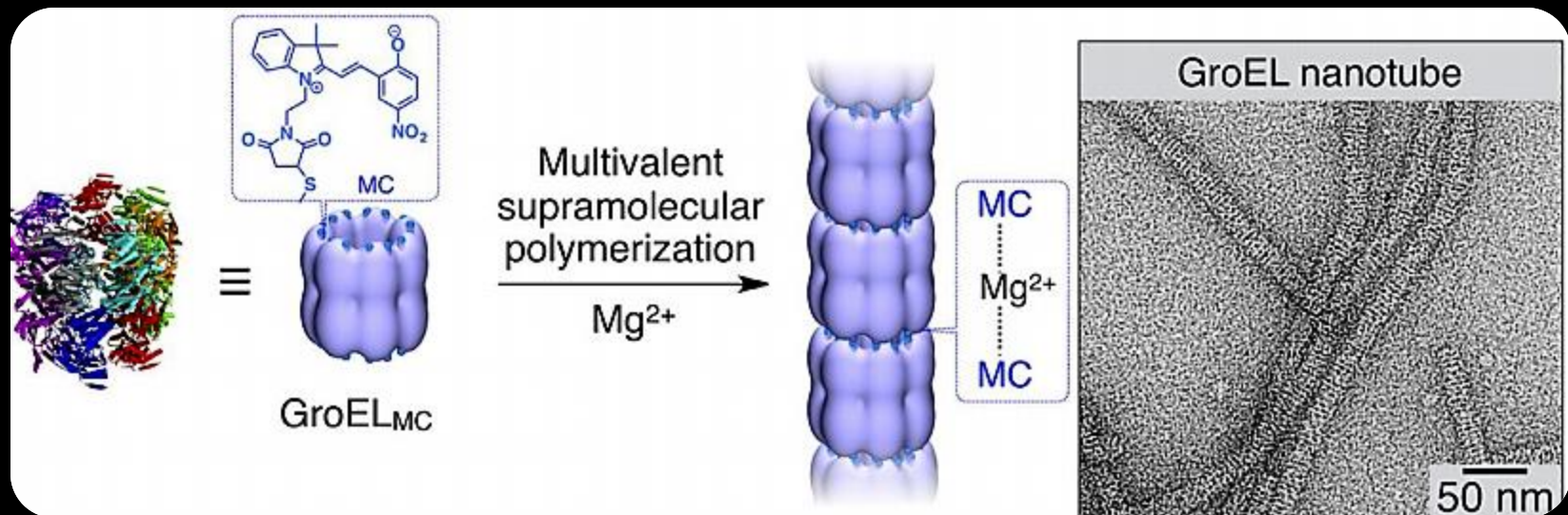
4. Conceptual expansion of supramolecular polymerization

4.1. Using unconventional monomers

- ✓ ATP-responsive biomolecular machines
- ✓ nanoscale inorganic objects with different dimensions

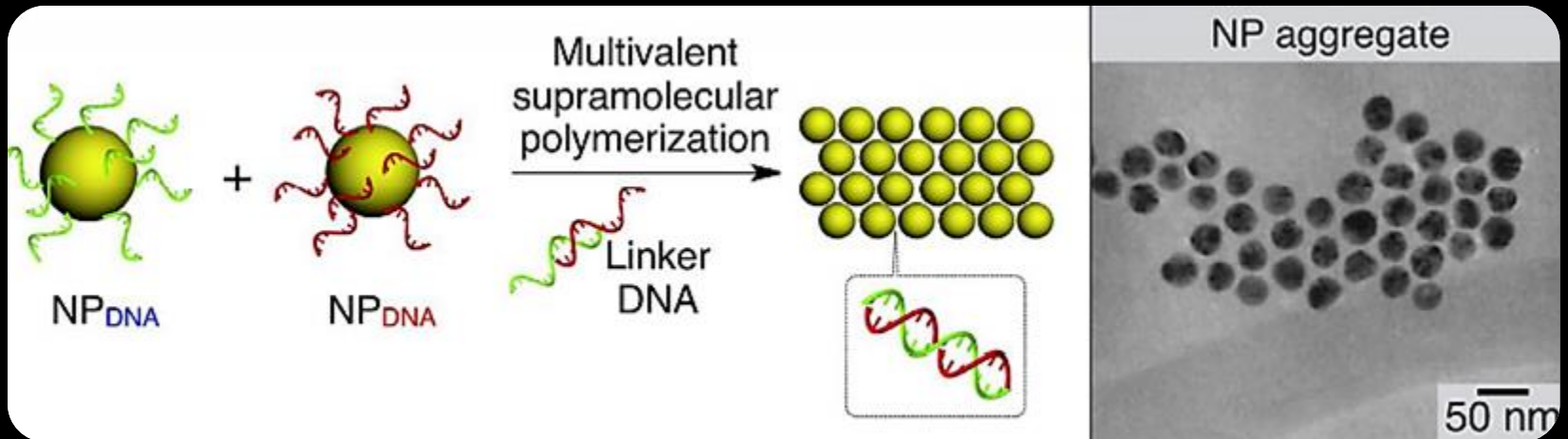
4.1.1. Biomolecular machines as monomers

GroEL adopts a barrel shape and assists in the refolding of denatured proteins with the help of ATP

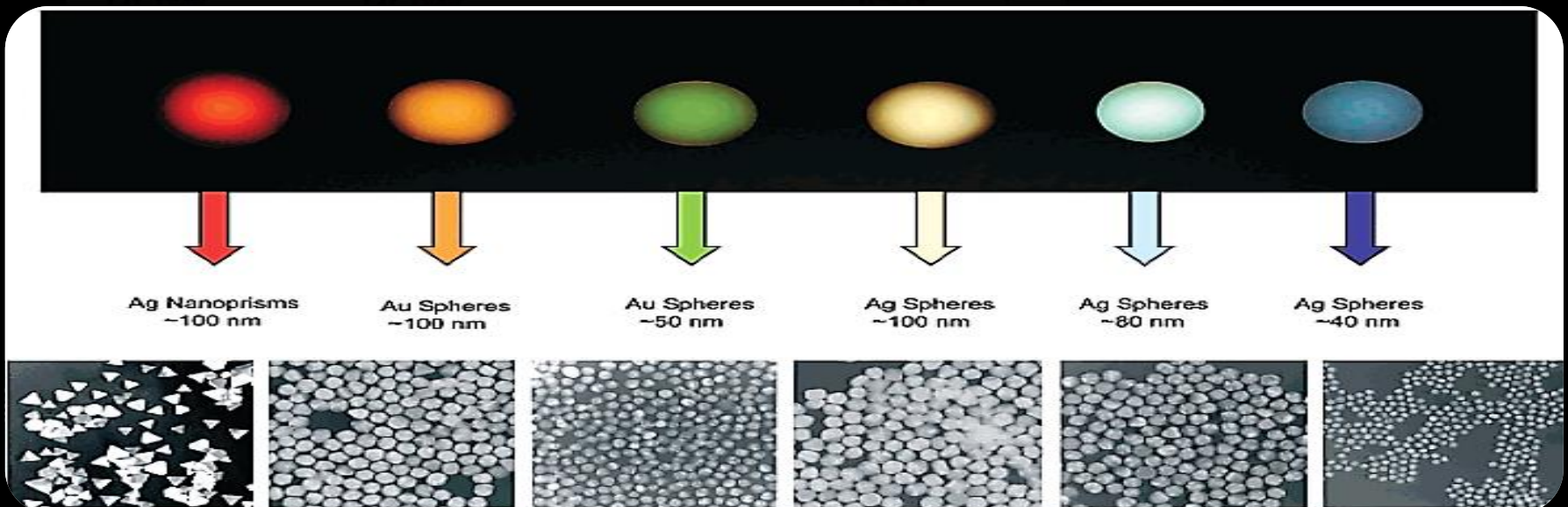


Multivalent supramolecular polymerization of biomolecular machines and nanoparticles. Schematic representations of GroEL with merocyanine-appended apical domains (GroEL_{MC}) and its 1D supramolecular polymer formed with Mg^{2+}

4.1.2. Nanoparticles as comonomers

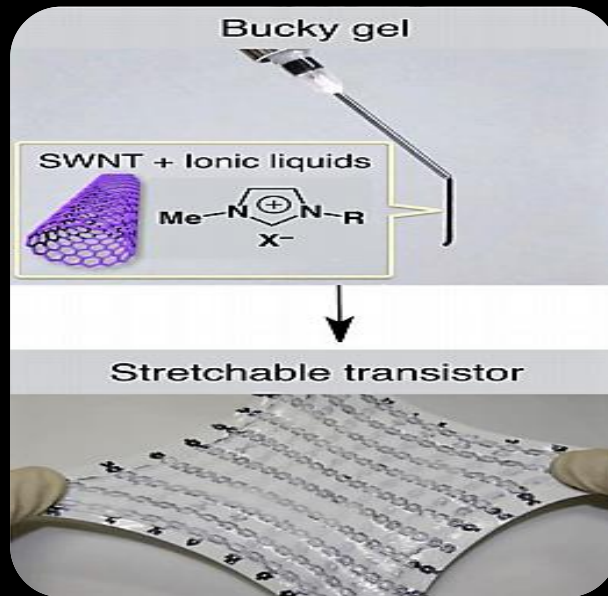


Multivalent supramolecular polymerization of biomolecular machines and nanoparticles. Schematic representations of DNA-appended nanoparticles (NP_{DNA}) and their multivalent supramolecular copolymers

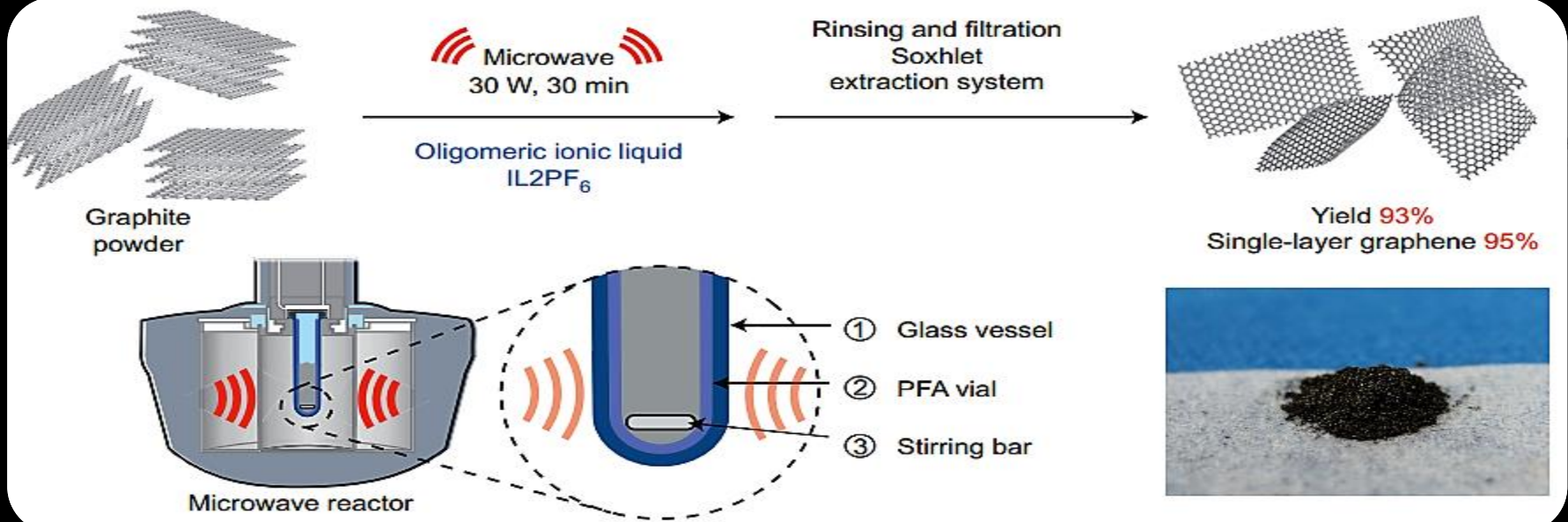


Sizes, shapes, and compositions of metal nanoparticles can be systematically varied to produce materials with distinct light-scattering properties.

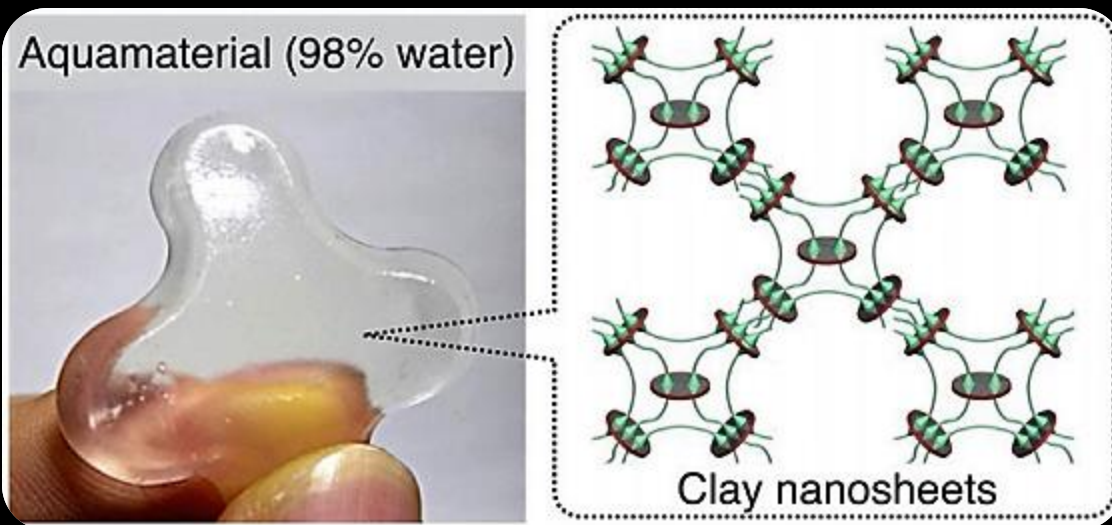
4.1.3. Nanotubes as comonomers



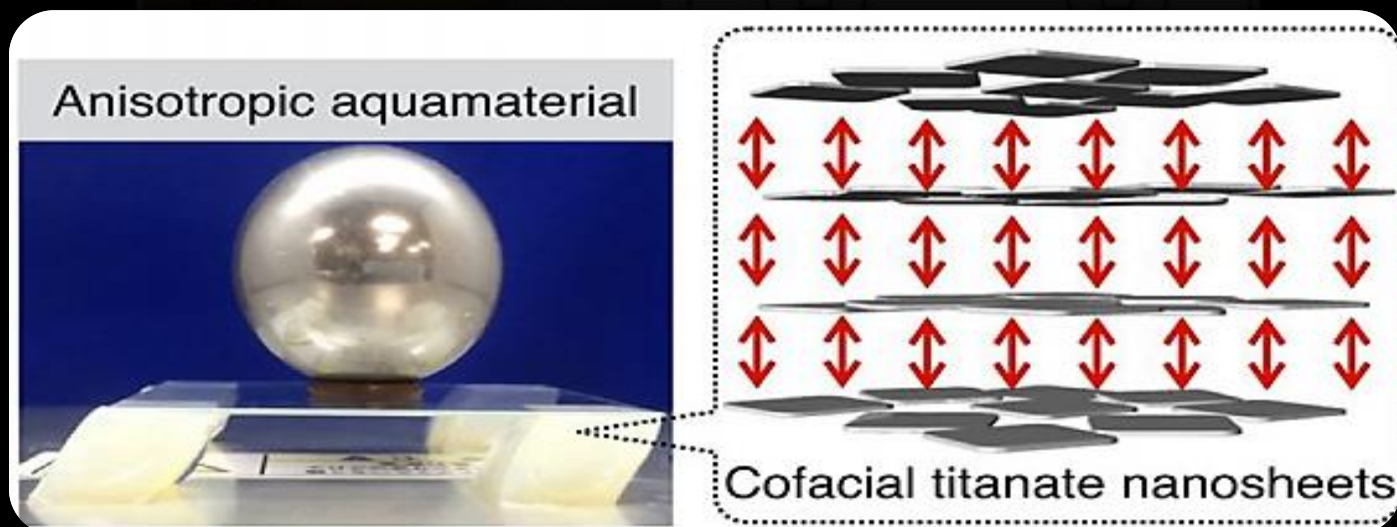
Supramolecular polymerization of unconventional monomers. Photographs of a bucky gel prepared by multivalent supramolecular copolymerization between CNTs and an ionic liquid and a stretchable active matrix transistor device fabricated with a bucky gel



4.1.4. Nanosheets as comonomers



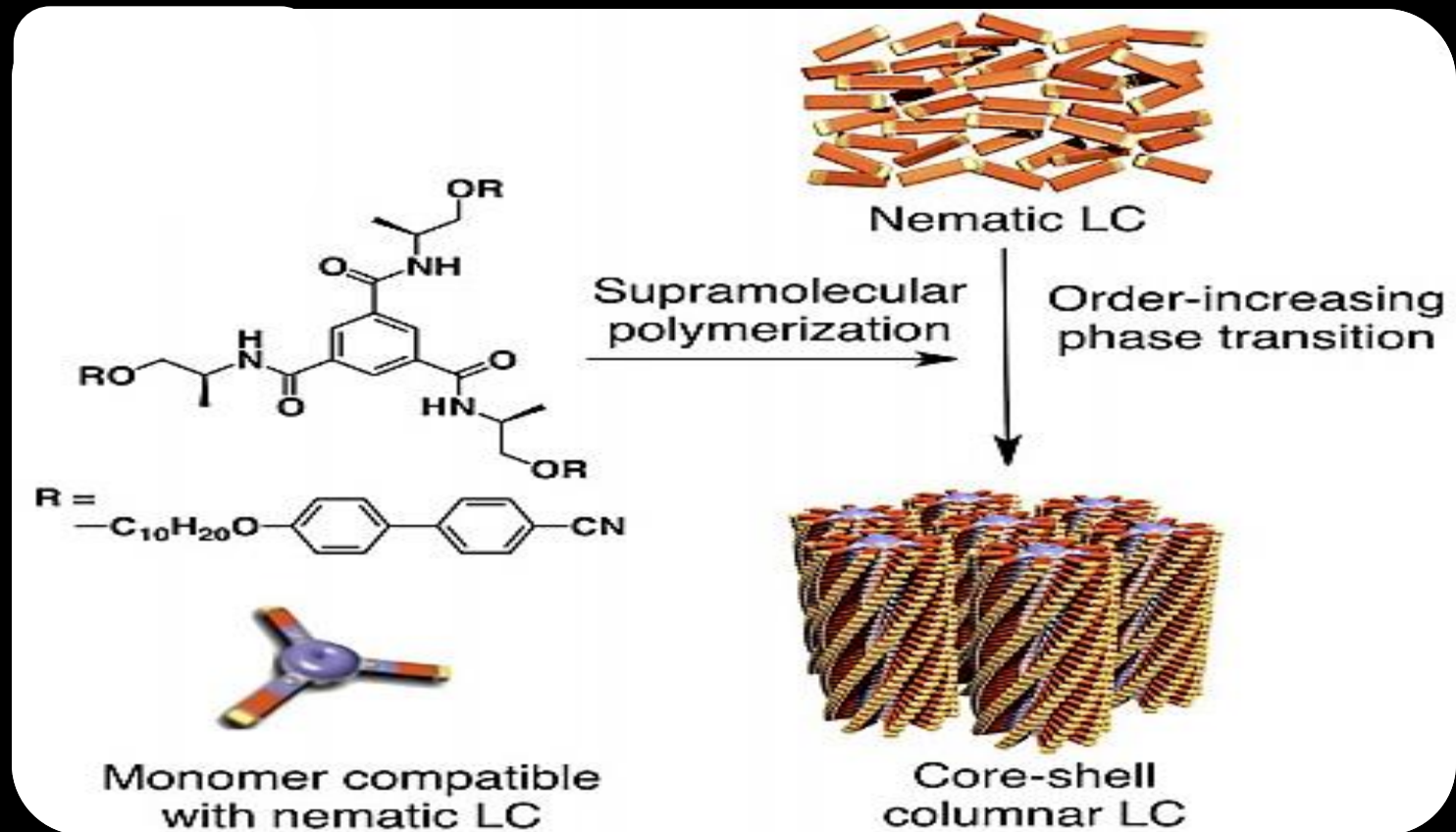
Photographs of a highly water-rich hydrogel called aquamaterial, prepared by multivalent supramolecular copolymerization between clay nanosheets and a dendritic molecular glue



Photograph of a highly anisotropic aquamaterial using magnetically oriented titanate nanosheets

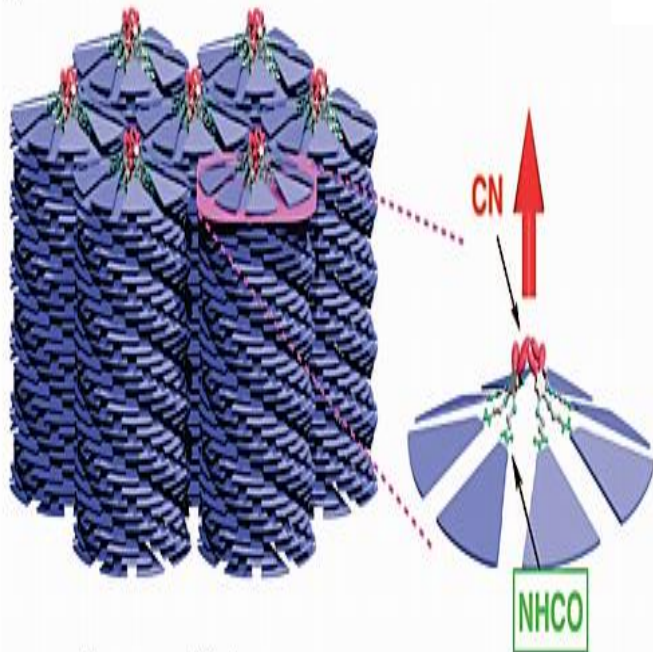
4.2. Supramolecular polymerization in unconventional media

4.2.1. In liquid crystalline media



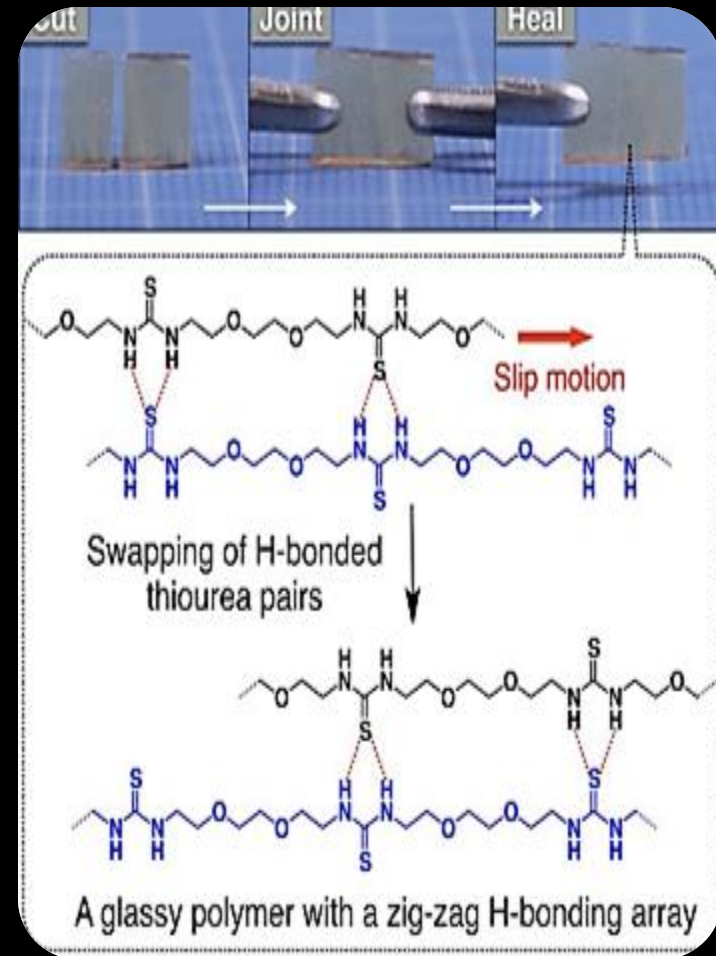
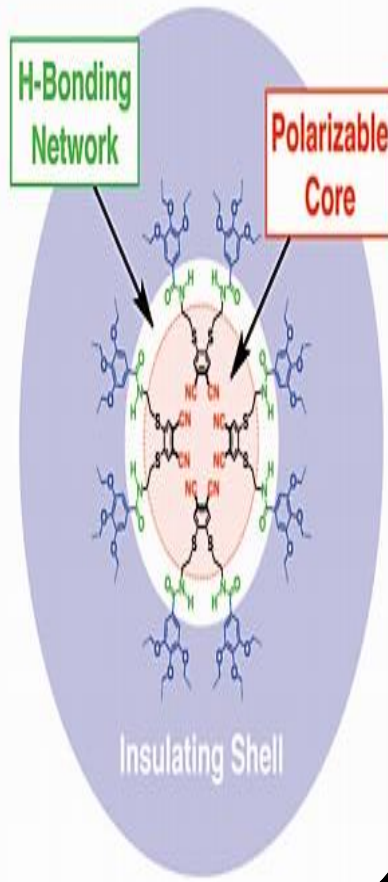
Chemical structure of a benzenetricarboxamide monomer and schematic illustration of its supramolecular polymerization in a nematic LC along with an order-increasing phase transition to a core-shell columnar mesophase

4.2.2. In bulk



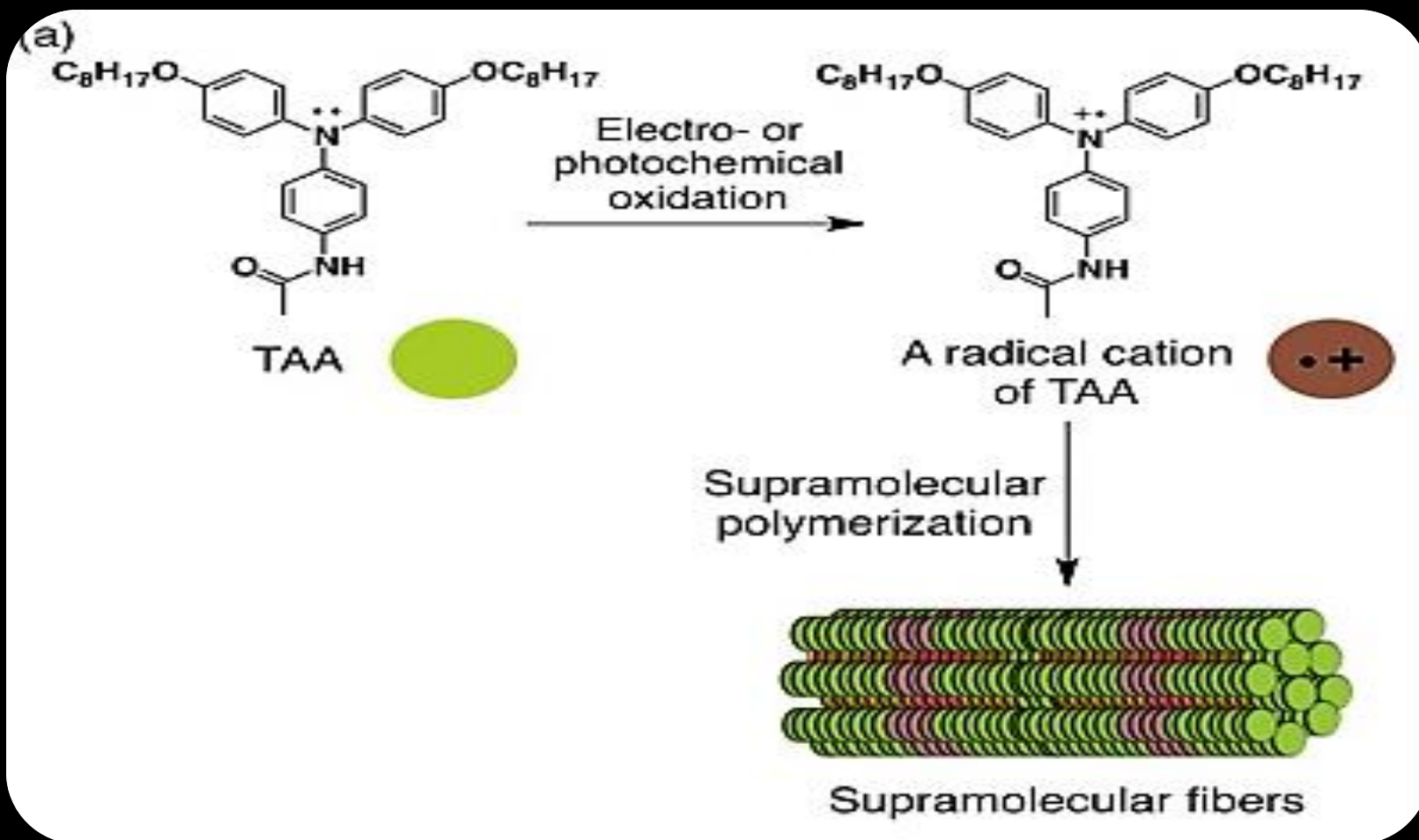
Hexagonal Columnar
LC Assembly

Umbrella Object



Photographs representing the self-healing event and healing mechanism of a glassy polymeric material obtained by multivalent supramolecular polymerization of oligomeric ether thiourea in bulk

4.2.3. On electrodes



Supramolecular polymerization on electrodes and at interfaces. Chemical structures of a triarylamine (TAA) monomer and its radical cation formed by electro- or photochemical oxidation, along with a schematic illustration of a fiber composed of the resulting supramolecular polymer