

Applications of supramolecular polymer networks

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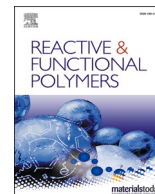
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Review

Applications of supramolecular polymer networks

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ABSTRACT

This perspectives article reviews selected key examples from the field of supramolecular polymer chemistry with the specific focus on the use of the dynamic properties that these materials possess in real-world applications. The scope of application for these fascinating materials, typically networks held in place by numerous weak, non-covalent bonds, has proven to be extremely diverse – significant effort in the past twenty years has enabled supramolecular polymers to now be found in developmental adhesives, batteries, anti-fouling coatings, healable barriers and regenerative medicines. Indeed, in recognition of the potential of these polymer chemistries, spin-out companies have been formed to exploit the commercial space that exists for materials with dynamic and reversible characteristics. The latter attribute is desirable in manufacturing materials and devices that can be recycled and reused.

1. Introduction

1.1. Supramolecular chemistry

The past four decades of science have witnessed how chemists have learnt from nature, in part by trial and error as well as elegant design, to understand and master the use of weak non-covalent interactions and self-assembly processes in synthetic systems to realise complex multi-component assemblies that exhibit attractive functionalities. To this end, Lehn's proposal that supramolecular chemistry is a new field where the scientific focus lies on the 'chemistry beyond the molecule' is now being borne out. It has enabled the realisation of a diverse array of molecularly assembled materials and complex mechanically-interlocked systems capable of, for example, switching behaviour and even doing physical work. The fundamental physical chemical and mechanistic details of this field are based upon the design of intermolecular complexes that are created via specific non-covalent interactions (metal-ligand interactions, hydrogen bonding, π - π stacking, electrostatic interactions, van der Waals forces). These topics have been extensively reviewed elsewhere so will not be covered in detail in this review [1–8].

1.2. Supramolecular polymers

The overlap of supramolecular chemistry with polymer synthesis in

the past thirty years has afforded a new class of materials – supramolecular polymers – that, on account of weak reversible non-covalent interactions within their assemblies, are dynamic in nature. Seminal studies in the early 1990's by the research groups of Lehn [9,10], Meijer [11–14], Stadler [15] took advantage of the strength of association between complementary hydrogen bonding units to afford stable supramolecular materials. The properties of these new materials were comparable to linear polymers possessing molecular weights far greater than the self-associating oligomeric units involved in the supramolecular network formation.

Molecular recognition units have been incorporated within macromolecular structures in several different ways to afford supramolecular networks, for example, at polymer chain ends [16], the termini of the arms of combs/brushes [17] or within the polymer main chain. In addition, the polymer architecture and number of molecular recognition units per polymer chain (referred to as the valency [18]) have also been adjusted to afford stable and processable supramolecular materials to permit multiple sites of association per polymer chain. In addition to these structural factors, phase separation between the recognition units, typically polar and apolar polymer blocks, has been shown to aid network stability [19,20]. The physical properties and mechanical characteristics of supramolecular polymer networks have been improved by a variety of strategies. In addition to enhancing the number of interactions per polymer chain, increasing the association

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(dimerization) constant of the recognition unit [21,22] and controlling the recognition dynamics [23] can lead to more strongly associated networks. The mixing of different polymers that feature mutually compatible recognition units has proven to be a successful route for generating stable supramolecular polymer blends [24–26]. Reinforcement of supramolecular polymer networks by using additives has also been shown to lead to property enhancement of this type of material [27–31].

These dynamic properties have been used advantageously to yield exciting materials that are, for example, stimuli-responsive and capable of autonomous repair [32]. This perspectives review highlights how supramolecular polymers have been utilised in a range of applications.

2. Applications of supramolecular polymers

2.1. Responsive adhesives

Designing adhesives that allow substrates to debond-on-demand (DoD) has become an ever more active field of research [33–35]. The drive for this technology is the increasing awareness of the need to account for the whole lifecycle of a product during the design and manufacturing process. Specifically, the requirement to recycle and reuse components and substrates that form complex consumer products be they automobiles, mobile phones or white goods. Traditional fixing techniques including welding, rivets and screw fixings are complex to automate to disassemble when the products have reached their end-of-life. In contrast, producing an adhesive that can debond in response to a specific stimulus allows for disparate materials (metals, glass, polymers) that have been securely assembled for the product's useful lifetime to be separated for efficient recycling.

Within the field of debond-on-demand polymers, the reversible nature of the supramolecular bond makes them ideal candidates to deliver debonding functionality [36]. A significant number of these debondable systems have now been realised, including those that can both i) reversibly bond and debond or ii) irreversibly debond once they have been exposed to a specific stimulus (Scheme 1).

An additional key factor in designing debondable adhesives is the selection of the debonding stimulus because it will constrain the utility of the final adhesive. For example, a typical hot melt adhesive can undergo debonding if the adhesive can be heated to a suitable temperature. However, this is often not practical because the adhesive may not be accessible or the substrates are not thermally stable or conductive enough to reach the temperatures required to melt the adhesive. This problem may be overcome by producing chemoresponsive adhesives or materials that respond to light, where no heat is required in either case. However, these solutions may also not be practicable if the required reagent cannot access the bond, or the substrates are opaque at the frequencies required to stimulate the polymer.

Nonetheless, the advance of debondable supramolecular adhesives continues at a pace resulting in a broad range of distinct solutions to the problem, as set out in the following sections using representative examples from the literature.

2.1.1. Thermally responsive supramolecular adhesives and materials

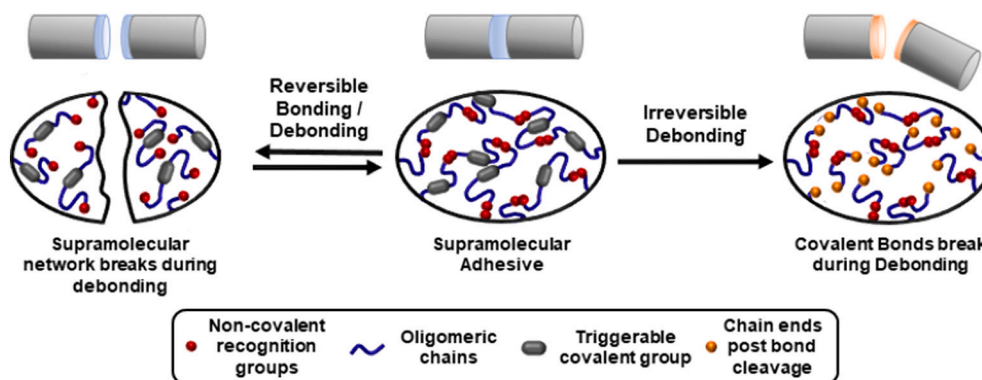
The inverse relationship between temperature and strength of supramolecular bonds has been well studied in the solution state. Indeed, the structural manipulation of supramolecular receptors on telechelic polymers to tailor their association constants has been demonstrated to dramatically affect the viscosity of the materials as a function of temperature in a broad range of supramolecular systems [2]. The reduction of viscosity of polymers with heat has been widely used in the adhesive industry to produce polyurethane hot-melt adhesives which flow sufficiently to be applied at elevated temperature then cool and solidify to form the bond [37]. In these systems, no new covalent bonds have been formed during the heating and cooling process, enabling the polymers to be reheated to facilitate debonding of the substrates.

Thermal debonding of supramolecular adhesives was exemplified [38] by Long and co-workers who synthesised a series of ureidopyrimidone (UPy) functionalised polyacrylates which showed adhesion to glass substrates (Fig. 1A). Higher loadings of the UPy group were found to afford stronger adhesion to a range of substrates. Similarly, the same group also developed adenine and thymine functionalised two-pot polyacrylate adhesives (Fig. 1B) which showed thermal reversibility of adhesion at 80 °C [39,40]. Using related functionality on a siloxane polymer backbone, Bosman and co-workers synthesised a UPy terminated siloxane that adhered to glass at 120 °C, and held a 1 kg weight for 24 hours without breaking [41]. If fractured, the adhesive could be re-adhered at 120 °C and was found to exhibit the same adhesive properties as the pristine bond (Fig. 1C).

2.1.2. Thermally debondable supramolecular adhesives without using conventional thermal heating

As noted in the introduction to this section, frequently heating a supramolecular adhesive to induce debonding is not practicable as the bonded components may be contained within a larger device, or the substrates may not be stable at the temperatures required. Therefore, significant efforts have been put into producing systems that can debond without heating the bonded substrates directly.

The addition of nano-composite fillers to supramolecular materials has been found to improve the physical properties of supramolecular materials [42,43]. Specifically, with respect to debond-on-demand adhesives, localised thermally induced bonding of substrates using metal nanoparticle composite adhesives has been shown to deliver quicker bonding times in comparison to traditional heating of the adhesive [44–46]. This adhesion method is possible by the incorporation of magnetic nanoparticles into the polymer network, which can be



Scheme 1. Schematic showing how the reversible nature of supramolecular bonds may be harnessed to produce a supramolecular adhesive, or irreversible debonding can be achieved by breaking covalent bonds.

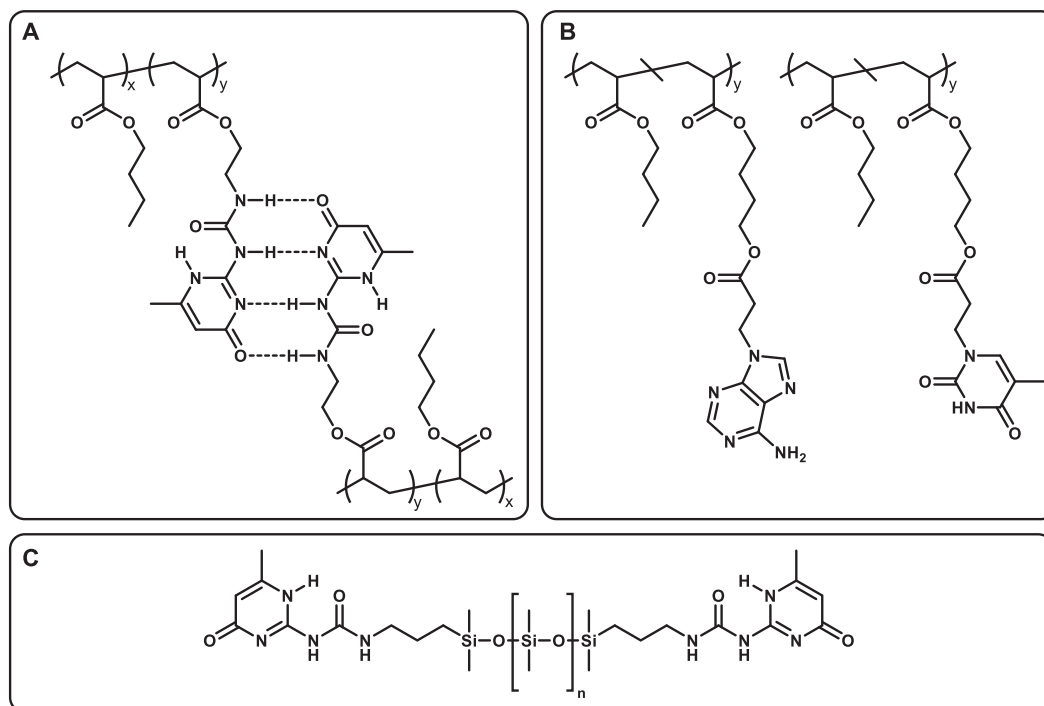


Fig. 1. The hydrogen-bonded supramolecular adhesives of (A) UPy functionalised and (B) adenine-thymine functionalised polymethacrylate co-polymerised with polybutacrylate developed by Long and co-workers [38–40]. (C) UPy functionalised polysiloxane used as an adhesive that is thermally reversible at 120 °C [41].

hysteresis heated through applying a high frequency oscillating magnetic field produced by an induction coil. However, reversing this method to induce debonding has only recently been reported [47,48]. Greenland and co-workers have shown that the use of iron nanocomposites imbedded in a supramolecular hydrogen-bonded polymer afforded rapid (<1 minute) debonding of glass substrates by hysteresis heating (Fig. 2). The material also exhibited excellent adhesion to metals, woods and plastics [48]. More recently, Meyer and co-workers demonstrated debonding metal plates using a commercial hot melt adhesive, where the bonded metal substrates rather than the adhesive underwent induction (rather than hysteresis) heating [49].

Weder and co-workers reported a conceptually distinct approach to localised heating of debond-on-demand adhesives. In this study a telechelic UPy functionalised polybutadiene was mixed with Tinuvin 326 [50]. Tinuvin 326 absorbs UV radiation efficiently, converting it to thermal energy which in turn heats the adhesive, resulting in a dramatic weakening of the polymer through dissociation of the hydrogen bonds in

the UPy dimers at *ca.* 70 °C (Fig. 3A). The material showed reversible adhesive properties without loss of strength both via light induced heating and direct thermal stimuli. Weder and co-workers also synthesised a benzimidazole pyridine ligand as an end group to a hydrogenated polybutadiene telechelic macromonomer (Fig. 3B) [50]. When bound to a zinc (II) ion, the macromonomer forms a supramolecular chain extended polymer. The material debonds from its substrates upon exposure to UV light, yet on removal of the radiation source, the metal-ligand interactions reform, and the original strength of the bond returns.

2.1.3. Reversible supramolecular adhesion using inclusion complexes

A reversible approach to debondable adhesives was shown by Harada and co-workers with their azobenzene functionalised glass surface [51]. With the azobenzene groups as the *trans*-isomer, the cyclodextrin (CD) based hydrogel adhesive would firmly adhere to the glass substrate. Switching the azobenzene to the *cis*-isomer by UV irradiation meant that the cyclodextrin ring could not bind to the azobenzene

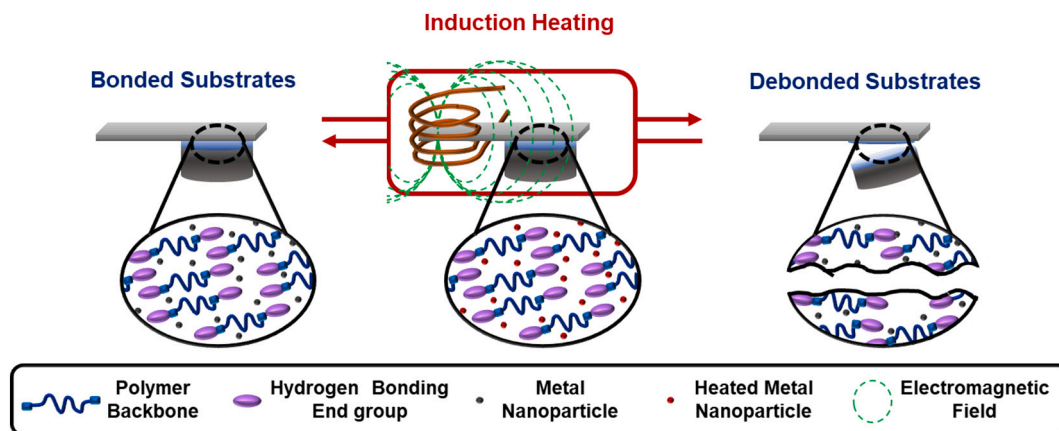


Fig. 2. Iron nanocomposite debond-on-demand adhesive developed by Greenland and co-workers [48]. The hydrogen-bonded supramolecular network debonds apart when exposed to an alternating magnetic field, which causes hysteresis heating of the iron nanoparticles [48].

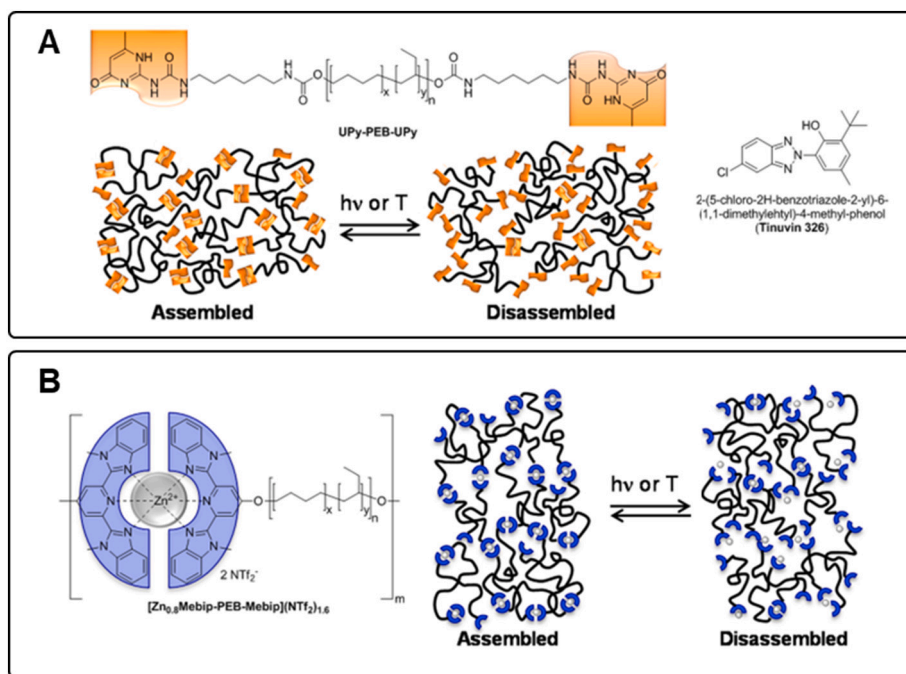


Fig. 3. (A) Telechelic UPy supramolecular polymer containing the dye Tinuvin 326. The dye absorbs UV light and re-radiated thermal energy, debonding the system; (B) Telechelic macromonomer relying on metal-ligand supramolecular interactions. The ligands radiate thermal energy when exposed to UV light, dissociating the metal-ligand interaction, weakening the adhesive material. (Adapted with permission from [50]).

groups, and hence the hydrogen adhesive does not adhere to the glass surface (Fig. 4). This is a conceptually distinct approach to achieve a debondable adhesive when compared to those described previously because the surface properties of the substrates are changed to cause debonding rather than manipulating the adhesive itself. The disadvantage to this method is that the surface needs to be functionalised prior to adhesion, and must have reactive groups that will allow for the attachment of the azobenzene groups. A conceptually similar use of inclusion complexes to form supramolecular polymeric adhesives was demonstrated by the Scherman group using the synthetic macrocyclic receptor cucurbituril [52].

A reversible approach to debondable adhesives was shown by

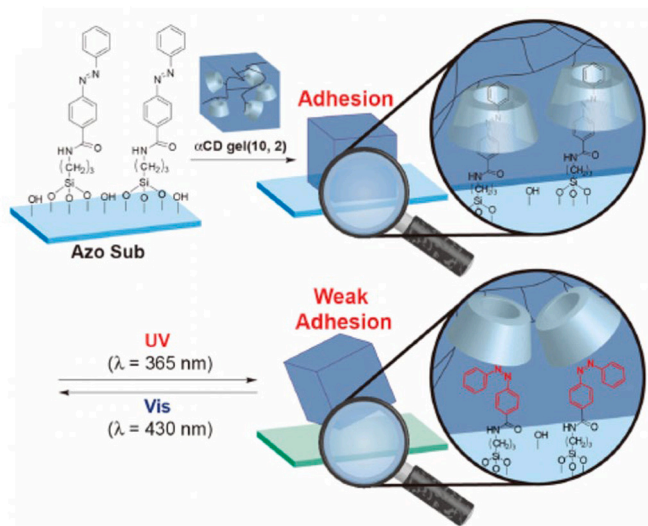


Fig. 4. Use of the inclusion complex between trans-azobenzene and an α -CD containing hydrogel. Switching between cis and trans states of the azobenzene on a glass surface changes the strength of the adhesion of the hydrogel to the substrate. (Reproduced with permission from [51]).

Harada and co-workers with their azobenzene functionalised glass surface [51]. With the azobenzene groups as the *trans*-isomer, the cyclodextrin (CD) based hydrogel adhesive would firmly adhere to the glass substrate. Switching the azobenzene to the *cis*-isomer by UV irradiation meant that the cyclodextrin ring could not bind to the azobenzene groups, and hence the hydrogen adhesive does not adhere to the glass surface (Fig. 4). Within the same study [51], the Harada group also showed reversible adhesion utilising the redox switching properties of ferrocene and binding within CDs. Similarly, Yan and co-workers employed electrochemical stimuli with poly(ionic liquid) strips functionalised with ferrocene and CD for reversible adhesion [52]. This is a conceptually distinct approach to achieve a debondable adhesive when compared to those described previously because the surface properties of the substrates are changed to cause debonding rather than manipulating the adhesive itself. The disadvantage to this method is that the surface needs to be functionalised prior to adhesion, and must have reactive groups that will allow for the attachment of the aromatic groups. Harada and co-workers further developed this approach by adhering hydrogels to one another utilising 2,2'-bipyridyl with CD and metal ions for potential medical and drug delivery application [53]. A conceptually similar use of inclusion complexes to form supramolecular polymeric adhesives was demonstrated [54] by Scherman and co-workers and Kim and co-workers [55] using the synthetic macrocyclic receptor cucurbituril.

2.1.4. Chemoresponsive supramolecular debond-on-demand adhesives

Chemoresponsive materials that respond to contact with chemicals have existed for many decades, with the most common method of changing the physical properties of the material by altering the pH of a chemoresponsive functional group (CFG) [56–58]. Altering the pH of the CFG is a reversible reaction and has been shown to enable functioning reversible adhesives as exemplified below.

Keddie and co-workers reported the use of an acrylic acid pressure-sensitive adhesive, which when exposed to basic conditions resulted in the deprotonation of the carboxylic acid [59]. This, in turn, causes the hydrogen bonding network of the acrylic acid to break down and allows the adhesive to peel away easily. Lawrence and Lapitsky presented the

use of an ionic hydrogel adhesive formed from the ionically cross-linked poly(allylamine) with pyrophosphate and tripolyphosphate [60]. The addition of sodium chloride promoted adhesion to glass and Teflon substrates, which could be reversed upon the addition of acid.

In contrast to these chemo-reversible systems, employing a non-reversible CFG within an adhesive has not been studied extensively. Using a non-reversible CFG allows for the irreversible depolymerisation of the polymeric network, hence allowing for a debondable adhesive. Phillips and co-workers showed the first chemo-degradable debond-on-demand adhesive, which degraded when it came into contact with a fluoride source, although this material was a crosslinked material rather than a supramolecular system [61].

Greenland and co-workers introduced [62] a fluoride responsive benzyl ether group developed by Turan and Akkaya [63] into a linear PU based hot melt adhesive that bonded at 160 °C. The adhesive underwent at least five bond/debond cycles without loss of bonding strength. In addition, it was able to undergo fluoride-initiated decomposition, resulting in a reduction of molecular weight from 26 kg mol⁻¹ to 6.2 kg mol⁻¹ resulting in a reduction in adhesion strength of approximately 40% (Scheme 2).

Later studies led by Greenland and co-workers showed [64] that the bonding and debonding temperatures could be manipulated by varying the composition of the backbone of the polymers. Introducing crystallinity into the system dramatically reduced the bonding temperature to 50 °C whilst retaining the irreversible fluoride degradation ability of the system. In addition, crosslinked variants could be synthesised (Fig. 5A) using a degradable CFG containing three benzylic positions (Fig. 5B), enabling the crosslinking points (yellow in Fig. 5A) to degrade in the presence of fluoride ions resulting in loss of adhesive strength [65].

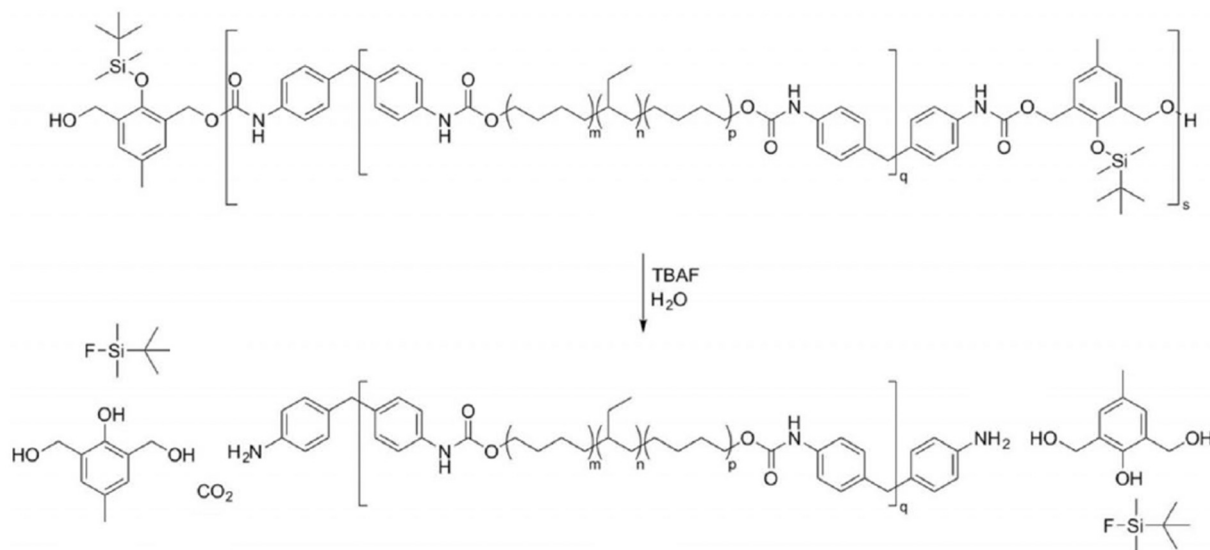
2.2. Supramolecular approaches to coating materials

To date, coatings based upon supramolecular structures have not been as extensively employed as their covalently cross-linked counterparts, presumably as their dynamic and ultimately reversible characteristics may not be practical for use long term surface protection systems. The use of supramolecular coatings does, however, provide the opportunity to impart self-healing properties [66,67], superhydrophobicity [68], and corrosion protection through the reformation of barrier properties after damage [69].

Self-assembled complementary supramolecular interactions have been used to generate water-swallowable materials that can self-repair upon surface puncturing [67]. Hayes and co-workers decorated linear

and tri-armed PEGs with a nitroaryleurea functional group capable of self-assembly. Blending the linear and tri-armed PEGs afforded supramolecular polymer networks that exhibited facile thermal repair at ambient temperature (20 °C) – films of this blend were cast onto glass slides and cut with a scalpel, in less than 30 minutes effective healing of the defect was observed. The supramolecular polymers could swell in an aqueous environment and thus provided surface contact between the two damaged and close a defect induced via needle puncture in the presence of water.

Schalley and co-workers have demonstrated how low molecular weight gelators (LMWGs) and their ability to form supramolecular polymer networks through hierarchical assembly has allowed them to be exploited as hydrophobic coatings when solution cast onto a surface [68]. A series of cyclohexane bisamides were investigated for their potential as coatings as these structures are excellent platforms for the generation of supramolecular polymers and gels [70–74]. Initial studies focused on assembling these gelator molecules in solution or gel states. A racemic diaminocyclohexane core was used, and the influence of the amide functional group, perfluorination, and length of the side chains was examined (Fig. 6a). When the side chains did not contain an amide functional group, irregular aggregates were observed in the films via SEM measurements, in contrast to the fibrous network formed in the presence of amide hydrogen bonding. A significant loss in the hydrophobicity was observed through contact angle hysteresis (CAH) and water static contact angle (θ_{stat}) testing. The amide functionalised gelators revealed increased hydrophobicity because of their hierarchical self-assembly through hydrogen bonding, and the gelators featuring perfluoroalkyl side chains exhibited superhydrophobicity ($\theta_{\text{stat}} \geq 150^\circ$) [75]. The length of the perfluoroalkyl chains was thus varied from three carbons (CF3) to seven (CF7), and it was found that the length of the chain was not a significant factor when comparing θ_{stat} , both gelators afforded super-hydrophobic surfaces in character. Interestingly, the CF7-based gelator provided a more stable surface covering when immersed in water (no damage was evident after three days) when compared to the CF3 gelator. Superhydrophobicity is not the only parameter critical in preventing wetting of a surface; low surface tension liquids like solutions of sodium dodecyl sulfate (SDS) exhibit much lower surface tensions than water and can thus wet super-hydrophobic surfaces. Surfactant airborne contamination would, therefore, prevent the coating from finding real-world application. The fibrous gel network was impregnated with a fluorinated lubricant (Fluornert FC-70), and significant improvement in the sliding angle was observed for the lubricated surface in comparison to the dried surface when testing a



Scheme 2. Fluoride initiated decomposition of the linear supramolecular hot melt adhesive produced by Greenland and co-workers [62].

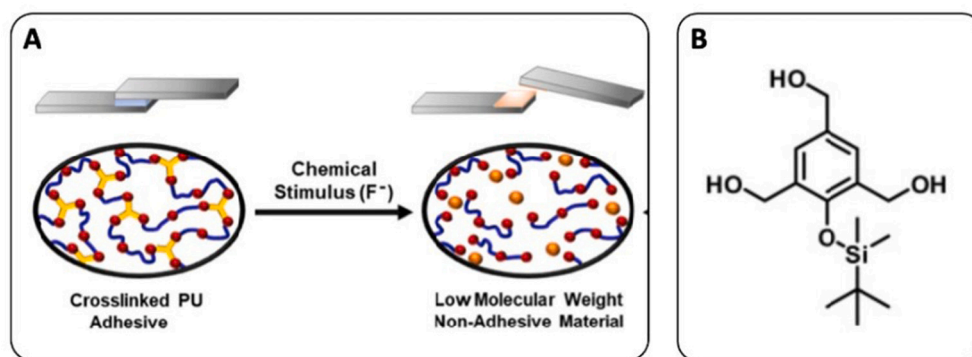


Fig. 5. (A) Schematic showing a chemoresponsive crosslinker (yellow) degrading on the addition of fluoride resulting in irreversible debonding of substrates; (B) Chemical structure of the fluoride degradable crosslinking monomer. (Adapted with permission from reference [65]).

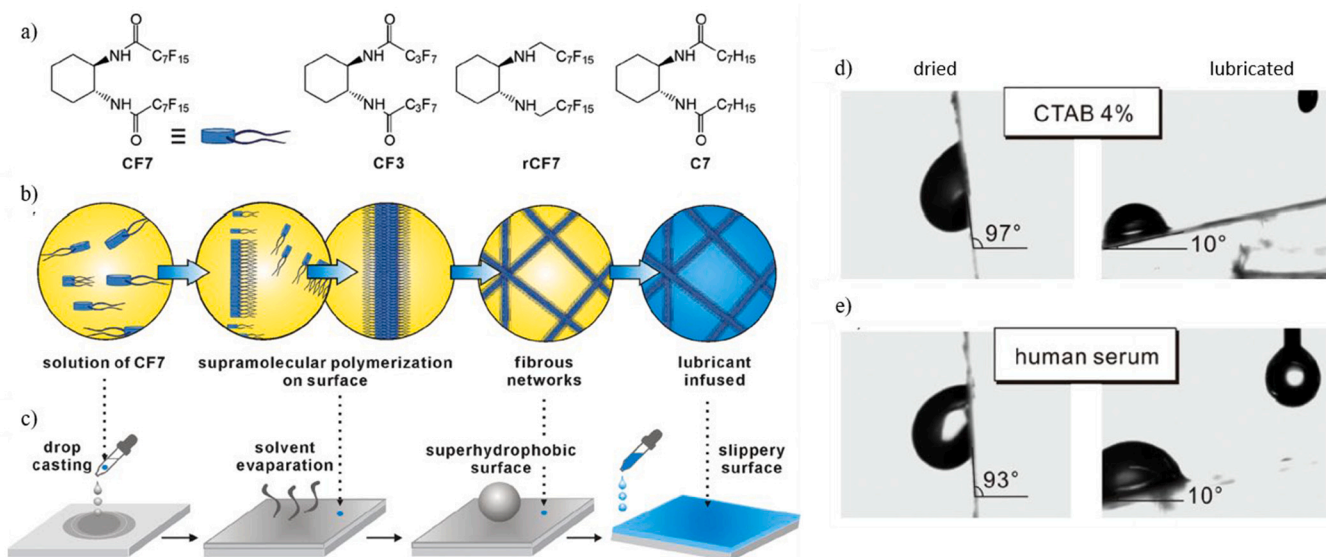


Fig. 6. a) Structures of LMWG CF7 and the control compounds CF3, rCF7, and C7. b) schematic illustration of supramolecular assembly on the surface of a material leading to the generation of fibrous networks. c) schematic illustration of the coating process to generate a superhydrophobic surface and subsequent impregnation with a lubricant. d,e) Wetting of dried and lubricated surfaces with a solution of CTAB 4% and human serum. Image reprinted with permission from reference [68].

solution of cetyltrimethylammonium bromide (CTAB), human serum, and water (Fig. 6d,e).

Hydrogen bonding motifs have found application in enhancing the mechanical strength, imparting healing, and adhesion of oil-repellent supramolecular silicone coatings. Taking advantage of a hydrophobic PDMS backbone, Yao and co-workers developed [76] a UPy functionalised siloxane supramolecular coating (Fig. 7) that had strong substrate bonding, a shear strength above 20 MPa for cellulose and metal substrates; the high shear strength was attributed to the strong hydrogen bonding between the UPy motifs and the surface functional groups (Fig. 7B). Within this study, the siloxane backbone's molecular weight was varied, and the overall mechanical properties of the coatings decreased as the length of the siloxane backbone was increased. CAH analysis indicated that coatings prepared with a siloxane oligomer with a molecular weight of ca. 870 a.m.u. exhibited the highest oil repellency with the lowest CAH values than coatings prepared with siloxane oligomers with a molecular weight of 3000 and 5000. The decreased oil repellency and higher CAH values of the higher molecular weight siloxane oligomers were attributed to microcracks in the coating's surface, as observed using SEM analysis, which acted as topographical defects. The healing properties were investigated by measuring the oil repellency of the coating before and after applying damage. By heating

the surface coating to 90 °C for 15 minutes, cooling, and subsequently measuring the CAH, the coating's oil repellency was shown to be maintained over 30 healing cycles.

When foreign objects are introduced into a body, non-specific protein adsorption occurs within seconds. A cascade of biological defence responses quickly ensue, neutrophils will interrogate the adsorbed proteins, and later macrophages will attempt to engulf the foreign object to degrade and clear it from the body [77]. Poly(ethylene glycol) has been used widely to impart protein and cell adhesion resistance [78]. Although this characteristic is not yet fully understood, it is proposed to arise from a multitude of factors: steric hindrance from compression of the PEG chains, hydrophilicity, chain length, and grafting density, as well as chain conformation [78–82]. A supramolecular grafting approach reported by Dankers and co-workers demonstrated [83] complete anti-fouling towards protein and cell adhesion through post-modification of a supramolecular UPy functionalised poly(ϵ -caprolactone) (PCL) elastomer. A UPy modified telechelic PCL formed the bulk of the elastomer. Mono, bi, and star PEGs were covalently attached to bicyclononyne (BCN) functional groups, which then were subject to an inverse electron density Diels-Alder cyclocondensation with a tetrazine functionalised UPy-PCL. The tetrazine functionalised UPy acted as an additive handle for surface insertion, and through supramolecular

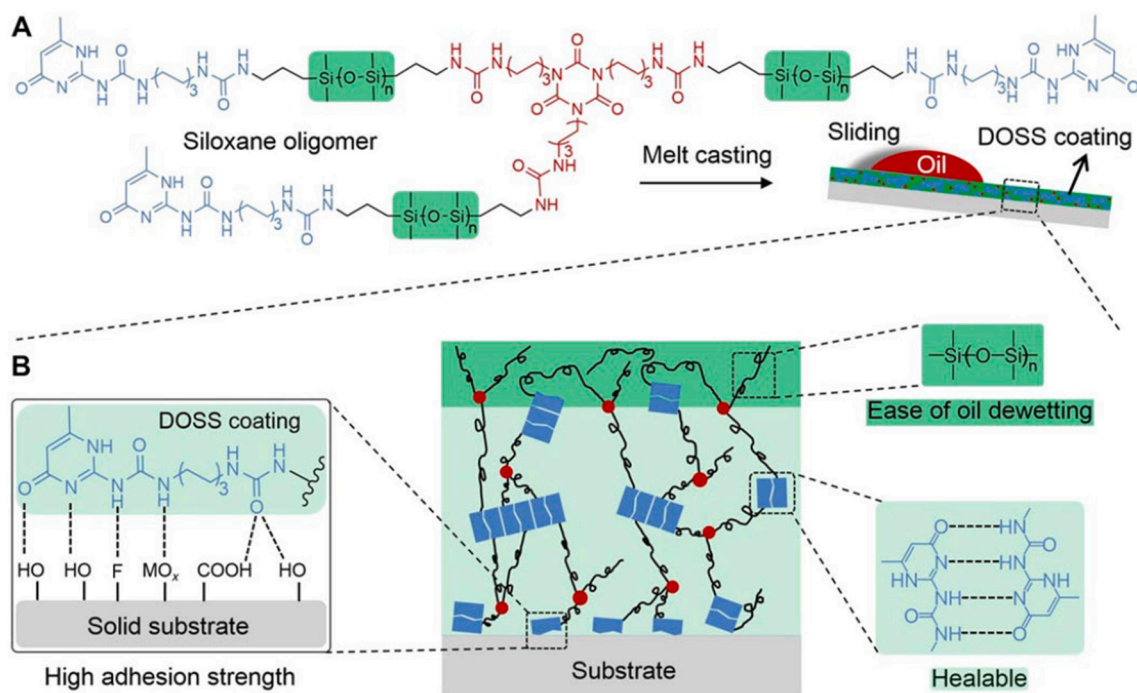


Fig. 7. A) Structure of tri-armed siloxane and preparation of damage-healable, oil-repellent supramolecular silicone (DOSS) coating. B) Schematic illustration of the hydrogen bonding between the substrate and the DOSS coating, enhancing adherence to various substrates. Image reprinted with permission from reference [76].

interactions of the UPy functional group, it is associated with the telechelic UPy modified PCL. Complete anti-fouling capabilities were afforded to the UPy telechelic polymer in the presence of the bifunctional PEG and the star PEG polymers, and a minor reduction in fouling was observed for the mono PEG derivative.

2.3. Use of supramolecular polymers in printing and additive manufacturing

Another exciting area that supramolecular polymers have found application in is printing [84] and additive manufacturing [85,86,87]. The molecular recognition between the macromonomers in supramolecular polymers forms *pseudo* high molecular weight materials. The low energy interaction between these macromonomers can be dissociated by heat or an appropriate stimulus. Therefore, these polymers can be regarded as discrete macromonomers in the melt or under specific conditions (depending on their association constant), allowing for their exceptional processability compared to conventional polymers. Deposition of the lower molecular weight materials decreases the chance of nozzle blockage during the printing process, reducing the printers' downtime and maintenance cost. Similarly, the deposition of supramolecular materials can increase the printing speed. Their tunability allows for the facile and controllable introduction of customised functionality based on the final application in biomedical, pharmaceutical, and food areas. Although the mechanical properties of these supramolecular polymer inks are generally inferior to conventional polymers, research is ongoing to develop suitable methods and strategies to produce robust and durable prints such as appropriate fillers [88–90] or the introduction of UV curable motifs [91]. This section provides an overview of notable examples of the 2D, 3D, and 4D printing of supramolecular polymers, specifically focusing on their applications [92,93].

2.3.1. 2D Printing using supramolecular polymers

Exploiting supramolecular polymer inks allows for the production of functional 2D prints. The printing industry can produce more than merely a depiction of letters, numbers. For instance, it can generate functional security inks [94,95], food packaging labels [96], or produce

coloured prints without using dyes [84]. For example, Schenning *et al.* have employed an ink formulation containing a UV-curable cholesteric liquid crystal and carboxylic acid hydrogen bonding motifs to print an optical battery-free humidity sensor for food and pharmaceutical packaging operating in the relative humidity range of 3 to 83% [96]. The reported functional ink can be inkjet printed, which changes colour reversibly from red to green based on the absorbed water content. After printing the hydrogen-bonded ink was UV cross-linked to retain the number of helical turns and the print thickness. By absorbing water, the printed polymer swells, increasing the helical pitch, reflecting light with a longer wavelength, and changing the apparent colour. Although the reported mechanism of the action could permit advanced and smart packaging, the quick reversibility of the colour change at temperatures above 0 °C could hinder monitoring the condition of the packages in transit and only represent the current status of the content. Furthermore, the incorporation of charge transfer complexes through supramolecular interactions has produced coloured inks [84]. Hayes and co-workers reported a double-component ink system, an electron-rich and an electron-deficient, which produce colours upon supramolecular cross-linking by taking advantage of π - π stacking interaction between the components [97]. The reported synthesised π -electron-rich component presents either pyrenyl or perylene terminal groups, and the π -electron-deficient component is a chain-folding naphthalene-diimide (Fig. 8). Subsequent inkjet deposition of the ink component on various substrates, including glass, steel and polycarbonate films, gave rise to red and green printed images upon forming a charge-transfer complex between naphthalene-diimide tweezer and pyrenyl or perylene, respectively (Fig. 8). In addition, the individual components of this ink were low molecular weight oligomers which reduces the risk of inkjet nozzle blockage, although in contrast, the self-assembled printed ink exhibited excellent mechanical properties such as durability and toughness [98]. The crosslinking of this ink's components was instantaneous and did not require any post-printing processes such as exposure to UV light or chemical triggers to realise the desired image.

Donor-acceptor and host-guest chemistry have also been reported to produce security inks enabling direct encrypted printing, which can be authenticated reversibly [94,95]. The fluorescent security ink reported

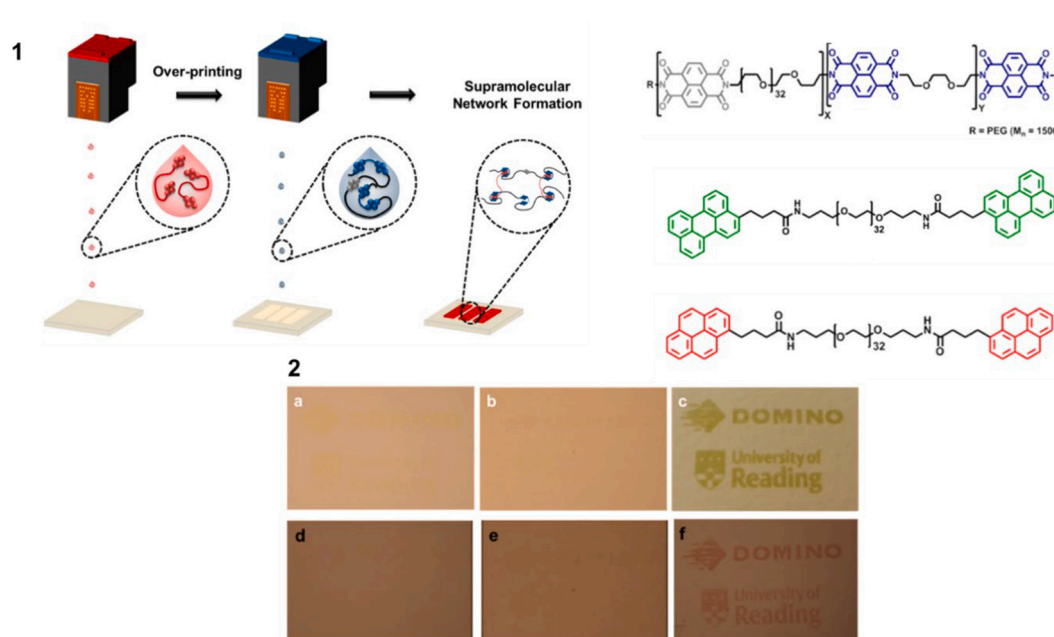


Fig. 8. 1) Schematic representation of the double-layer printing approach and the structures of the individual components of the ink (Blue: the π electron-deficient component and green and red: the π electron-rich components). 2) (a,d) printed single component pyrenyl and perylene inks, (b,e) printed single component naphthalene-diimide ink (c,f) overprinting of the inks to create colour at ambient condition. Image reproduced with permission from references [84, 97].

[95] by Stoddart and co-workers is a rotaxane-based formulation capable of producing a pallet of finely tuned colours by varying each component's concentration in the formulation. This formulation consists of different host/guest moieties (for example, γ -cyclodextrin, adamantylamine), which compete with complex formation between the rotaxanes pyrene and γ -cyclodextrin units. The rotaxane γ -cyclodextrin complex was responsible for producing different fluorescent colours by changing the molar ratio of the bound α -cyclodextrin to the rotaxane (Fig. 9).

2.3.2. Realisation of 3D printed images employing supramolecular polymers

3-Dimensional (3D) printing/additive manufacturing is defined as the layer-by-layer production of a 3D component. 3D printing and supramolecular polymers can potentially be used synergistically. For example, the high shear and velocity involved in a 3D printing process facilitate the directing of the supramolecular motifs to align the microfibrils or aid the microphase separation. This is not easily and reproducibly achieved in other production methods such as drop casting or moulding. The combination of the tunability of the supramolecular

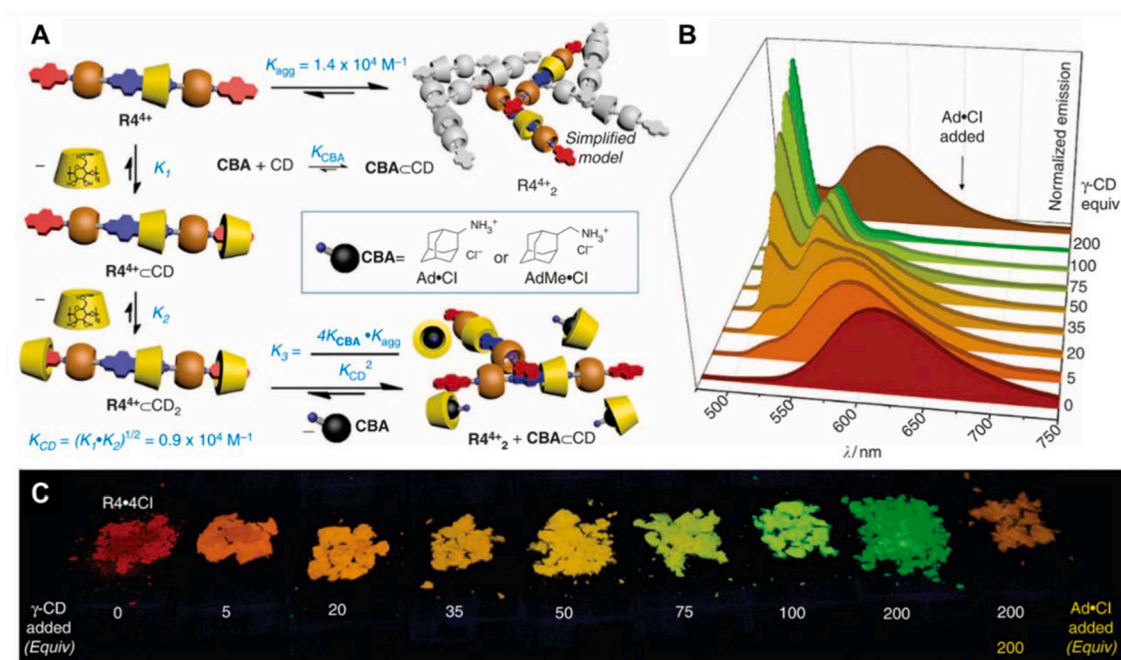


Fig. 9. A) Graphical representation of the rotaxane ink's action mechanism reported by Stoddart et al. and the competing guest species' role. B) Solid-state fluorescence spectra of the rotaxane ink with a different equivalence of γ -CD inclusion complex generated by λ excitation = 347 nm. C) The variety of colours produced by a mixture of the rotaxane ink containing different amounts of the inclusion complex under UV light. Image reproduced with permission from reference [95].

polymers and 3D printing as a readily customisable production method has contributed considerably towards progression in the biomedical field, which will be discussed in more detail in the following section [99–101].

Melt extrusion additive manufacturing is a direct additive manufacturing technique that requires minimal chemical/physical alternation to deposit material. Therefore, it is a highly desirable method for producing pharmaceuticals [102,103] and where the purity and non-toxicity of the material are of high importance. The development of new polymeric materials suitable for hot-melt extrusion is understudied, and currently, there are limited types of commercially available materials/filaments, namely poly(lactic acid) (PLA) and acrylonitrile-butadiene-styrene copolymer (ABS). Supramolecular polymers are emerging in melt extrusion 3D printing as a result of the advantages they bring, such as lower processing temperature [101], superior mechanical properties, better interlayer adhesion, rapid polymer solidification [104] and readily tuneable mechanical properties [85]. For example, Long and co-workers have reported developing a segmented supramolecular polyurea exploiting ureido-cytosine with a quadruple hydrogen bonding as the molecular recognition motif [104]. The quadruple hydrogen bonding results in an outstanding toughness modulus of *ca.* 81 MPa in a printed supramolecular polyurea, which could be elongated to 1200% of its original length. A physically cross-linked network controls the mechanical properties of the material. In fact, upon a 50 °C increase in the temperature from 120 °C to 170 °C (around the dissociation temperature of the hydrogen bonds), the material's viscosity drops by three orders of magnitude can be reversed rapidly upon cooling down. This substantial drop in viscosity and the ability to regain it rapidly made this supramolecular polyurea a suitable candidate for hot-melt extrusion 3D printing. It has been demonstrated that the rapid solidification of the material enabled the deposition of small single-walled geometries (Fig. 10A). Additionally, a similar segmented supramolecular polyurethane has been reported by Hayes and co-workers to print a customised drug-release implant at a lower temperature, allowing for the incorporation of a wider variety of drugs with lower decomposition temperatures (Fig. 10B) [101].

2.3.3. Accessing 4D printed structures via use of supramolecular [polymers]

Implementation of responsive supramolecular materials as inks has permitted 4D printing. 4D printing is defined as 3D printing of a part that can undergo shape change in response to an appropriate stimulus

after being printed. Introducing a reversible shape change to this technology advances the field and enables the production of ever more complex structures which can perform a task. Ware and co-workers proposed an azobenzene liquid crystal supramolecular elastomer that can be 4D printed as a Braille-like actuator (Fig. 11).[105] The proposed material comprises four key functionalities: mesogen to achieve crystallinity, azobenzene to induce shape change, Diels-Alder adduct to provide the processability needed for extrusion printing and 2-ureido-4 [1H]-pyrimidinone (UPy) to lock the aligned structure after shape change using quadruple hydrogen bonds. The printed Braille sheets consist of 6 dots, which can be raised accordingly upon temporary irradiation with UV light. The raised shape is stable for 24 hours and can be returned to the original flat structure by heating the image to 65 °C to adopt a new form (Fig. 11).

Lu and co-workers reported a polyethyleneimine-co-poly(acrylic acid) synthesis that forms metallo-organic coordination with Eu^{3+} ions to produce a range of luminescence colours [106]. A bilayer shape was printed consisting of a non-swelling polymer layer and a layer of the reported metallo-organic supramolecular hydrogel. The bilayer printed material showed luminescence colour change, opacity, and shape changes by tuning the ratio of coordinated and free Eu^{3+} ions and the degree of swelling in water. By taking advantage of these characteristics, successful printing of an underwater soft-grip actuator (which was invisible to marine life) was realised to grab and hold objects with a force of 0.16 N (Fig. 12).

2.4. Supramolecular healable polymeric materials

A polymeric material's ability to heal any damage in either an autonomous way or via the application of a mild stimulus is an extremely attractive proposition. The global focus on environmentally friendly uses of polymeric materials has meant that minimising maintenance costs, reducing environmental waste and ultimately extending a material's lifespan by learning how to make polymers healable are sufficient reasons to justify the extensive research on this topic in the past decade. Prototype healable polymer systems have found applications in areas ranging from the healthcare industry [107] to anti-corrosion coatings [108], and flexible/wearable electronics [109–113].

The introduction of supramolecular interactions in polymer chemistry generates *pseudo* high molecular weight polymers, and as such, they can display mechanical properties consistent with those of high

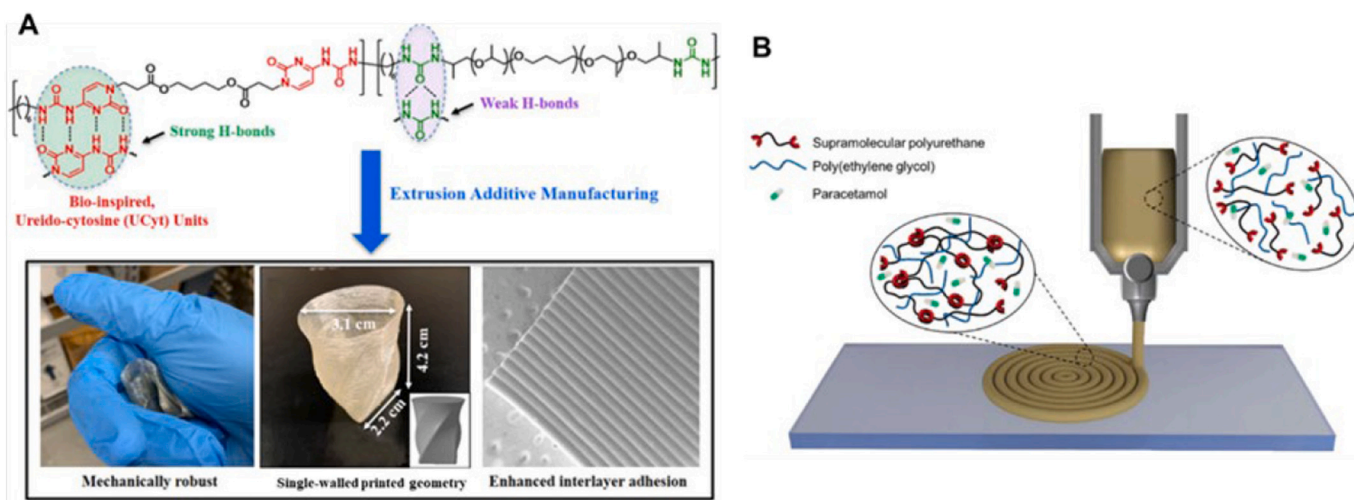


Fig. 10. The segmented polyurea reported by Long and co-workers showing the A) chemical structure featuring the quadruple hydrogen bonding and the properties of the printed part including its superior mechanical properties, the rapid solidification of the material upon deposition, which enables the production of small single-walled structures, the efficient interlayer adhesion resulted from the polyether low T_g and the physical cross-linking from UCyt. B) Hot-melt printing process of the supramolecular printed implant reported by Hayes and co-workers. The images in A) and B) are reproduced with permission from references [104] and [101], respectively.

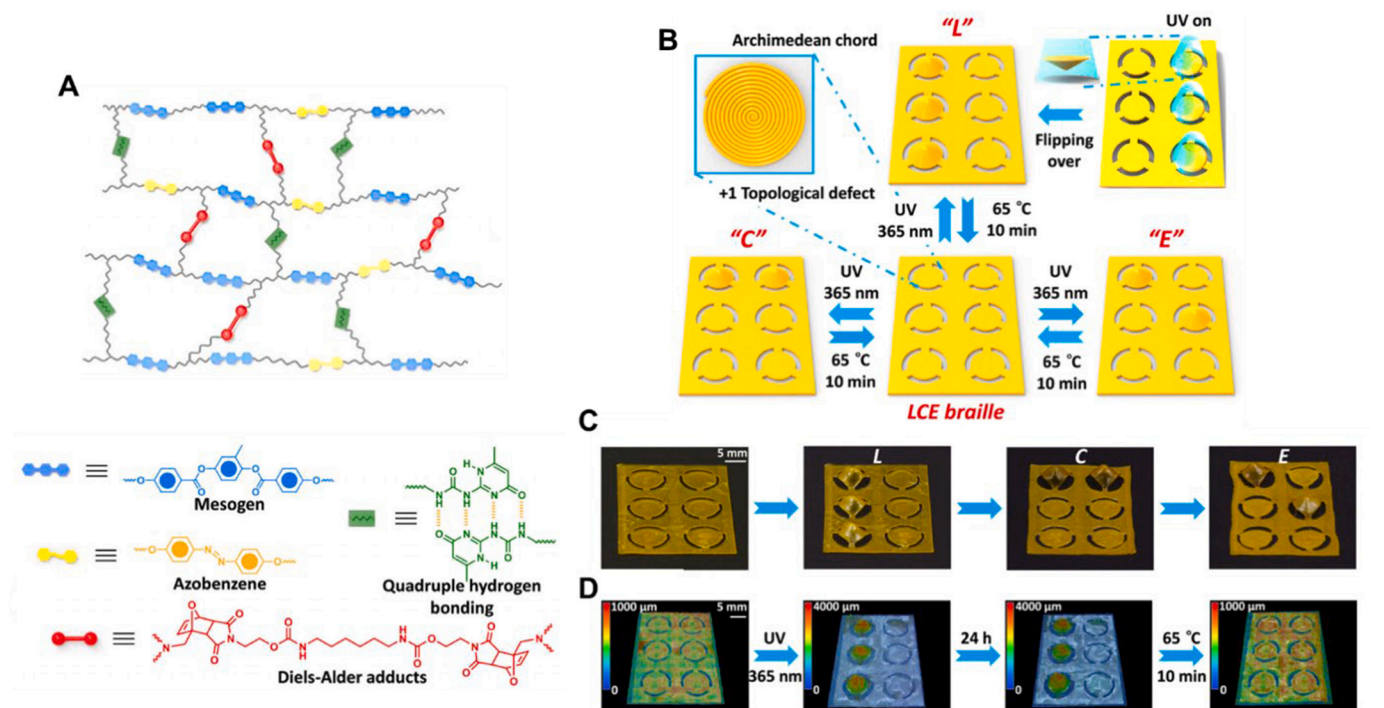


Fig. 11. A) Schematic representation of the chemical structure of the azobenzene liquid crystalline supramolecular elastomer. B) Illustration of the 3D printed Braille-like sheet designs. C) Images of the printed Braille sheets showing letters "L", "C", and "E" 24 h after UV irradiation. D) Micrograph topography of the printed Braille sheet during one cycle of the reversible shape change. Image reproduced with permission from reference [105].

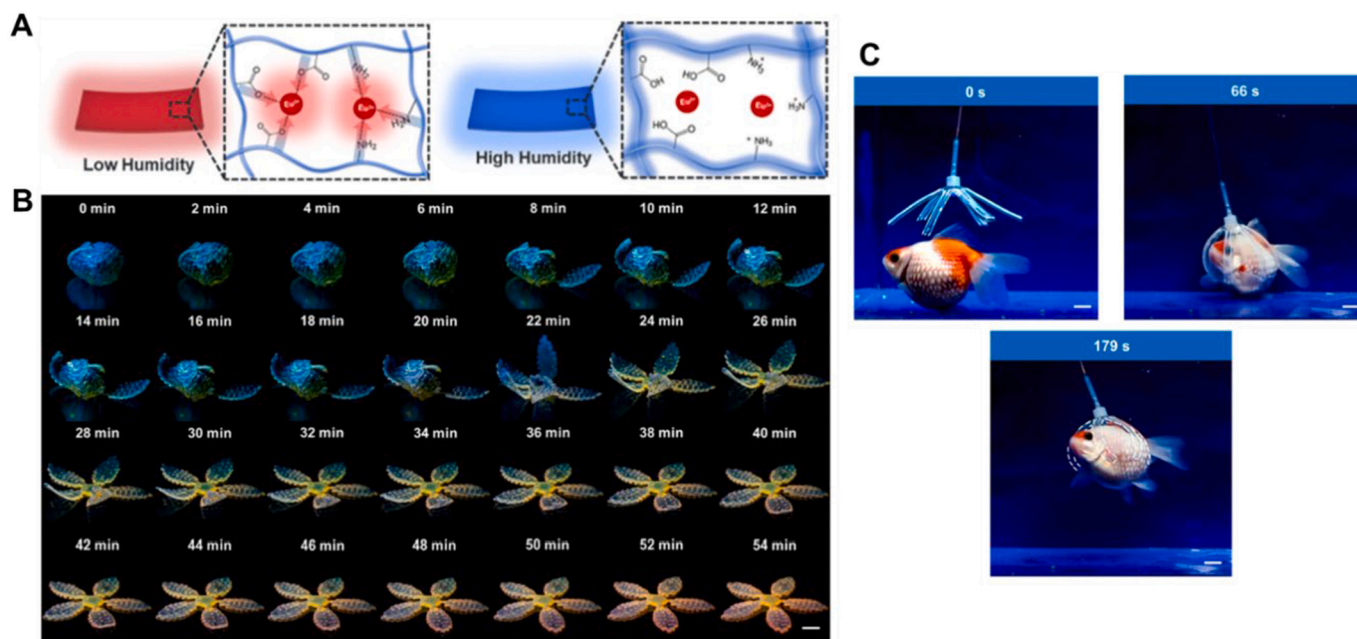


Fig. 12. A) Mechanism of colour change by increasing the humidity. B) Progressive images of a fully swollen printed flower (at a relative humidity of 20%). The shape is drying slowly over time; thus, the material is becoming less swollen, and the flower is blossoming as a result. $\lambda_{\text{excitation}} = 340 \text{ nm}$ for colour change monitoring. C) Images of the soft-grip actuator in action. As the part is submerged in water becomes transparent (swollen and less phase-separated). Image adapted with permission from reference [106].

molecular weight polymers. Furthermore, supramolecular interactions allow the polymer network to be temporarily broken into shorter polymer chains upon exposure to suitable stimuli and consequently facilitate intrinsic healing mechanisms through increased chain mobility and dynamic bonding. Excellent reviews by Simon and co-workers plus Binder and co-workers have provided excellent coverage of the

fundamental mechanisms and properties of supramolecular polymers [114,115]. The opportunity to tune the mechanical properties of polymeric materials and the reversibility of dynamic bonds has led to self-healing materials finding their way into real-world applications.

2.4.1. Healable hydrogen bonded supramolecular polymer materials

In 2008 Leibler and co-workers published [116] the first use of primarily hydrogen bonding interactions to generate a supramolecular network capable of self-healing. The elastomer, commercialised subsequently by Arkema under the name Reverlink™, utilised a mixture of fatty diacids and tri-acids, which were reacted in sequence with an excess of diethylenetriamine and then reacted further with urea to produce a mixture of oligomers with hydrogen bonding receptors (Fig. 13) [117–122]. The amidoethyl imidazolidone, di(amido ethyl) urea, and diamido tetraethyl triurea functional groups behaved as the hydrogen bonding sites within the disperse product to facilitate the formation of a network. Upon heating the material to 90 °C (above the glass transition temperature, $T_g = 28$ °C), the network material exhibited soft elastomeric properties with a strain at breaking of 350%. Additionally, complete elastic recovery was obtained up to 100% strain, and at temperatures above 160 °C, the material behaves as a viscoelastic liquid and can be extruded. The glass transition temperature was lowered ($T_g = 8$ °C) using a plasticiser to obtain a material that behaved as an elastomer at room temperature. The use of low molecular weight oligomers that self-assemble represents a unique pathway towards self-healing supramolecular polymer networks. Reverlink™ has since found application in the fabrication of self-healing stretchable wires [123]. In this use, the elastomer was heated to 60 °C and poured into a mould containing a single copper wire. The mould was then cured at 120 °C for 48 hours, and the copper wire was removed to produce a microchannel. This microchannel was subsequently injected with a liquid alloy eutectic gallium-indium (EGaIn) to produce a conducting wire that can be cut and rapidly self-heal at ambient temperatures.

Yanagisawa and co-workers have reported [124] a series of mechanically robust amorphous poly(ether-thioureas) and found that although the polymers contained many hydrogen bonding units, the material would remain amorphous because of the non-linear thiourea arrays. In contrast, it was found that the analogous urea polymers were semi-crystalline (Fig. 14). The less ordered thiourea arrays do not crystallise and, in combination with low molecular weight polymer chains, thereby facilitating chain motion, led to the development of a polymeric material capable of self-healing with compression in the absence of heating.

Stable supramolecular assemblies form because of strong complementary non-covalent interactions and controlling these associations' strength is critical when designing dynamic and responsive polymeric

materials. Meijer, Sijbesma and co-workers modified telechelic polymers such as polysiloxanes [16] and poly(ethylene-co-butylene) [125] with ureidopyrimidones (UPy); the introduction of the UPy end-cap to telechelic polymers has resulted in the manufacturing of commercial, thermoreversible, supramolecular polymer materials by SupraPolix BV [126–135]. Lamers *et al.* recently illustrated the significance of association strength by functionalising a poly(dimethylsiloxane) (PDMS) polymer backbone with three different supramolecular moieties that vary in association strength [136]. A dinitrohydrazone (hyd) moiety was chosen as it associates through weak supramolecular interactions such as π - π stacking afforded a viscous material at room temperature. In contrast, when more robust self-associating motifs were used, e.g., benzene-1,3,5-carboxamides (BTA) and UPy, which can assemble via more potent triple and quadruple hydrogen bonding, materials with significantly different physical properties were produced. A thermo-plastic elastomer was generated in the case of the BTA functionalised PDMS, and functionalising PDMS with UPy units afforded a very brittle material such that high-temperature compression moulding (130 °C, 100 bar, 20 minutes) was required to reprocess the material. The dynamic properties of the polymers were probed through stress relaxation experiments. In the cases of the hyd- and the BTA-functionalised PDMS polymers, complete stress relaxation was achieved in 160 and 210 seconds, respectively. However, in the case of the UPy grafted polymer, more than 8 hours was required to obtain complete stress relaxation. This study elegantly highlights the importance of understanding and controlling the strength of association of the supramolecular receptor as efficient stress relaxation is a function of the supramolecular network's reversibility and the relaxation of the polymeric chains that have undergone stress. Supramolecular interactions, being dynamic, allowed the materials generated to be reprocessed without loss in mechanical properties, whereas, in the instance of covalently cross-linked materials, if the covalent bonds are broken because of mechanical damage, then recovery of the original mechanical properties of the pristine material requires an external healing agent.

2.4.2. Metallosupramolecular healable polymer systems

Rowan, Weder and co-workers have illustrated how tough and optically healable supramolecular polymers can be generated through reversible metal-ligand coordination chemistries [137]. A low molecular weight telechelic poly(ethylene-co-butylene) core was functionalised with 2,6-bis(1'-methylbenzimidazolyl) pyridine (Mebip) ligands and

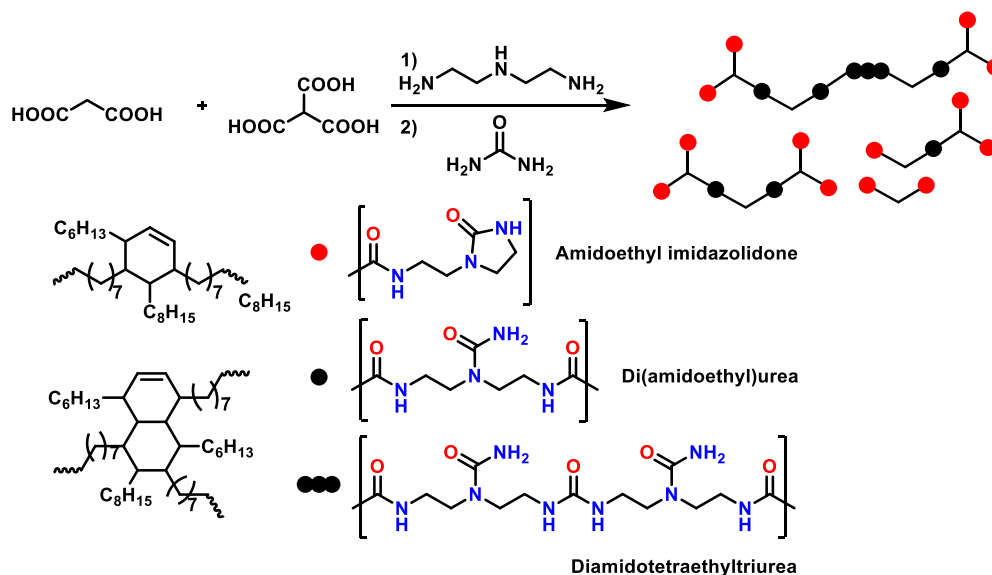


Fig. 13. Schematic representation of the synthesis of Reverlink™ [116], a disperse mixture of oligomers that is responsible for its unique mechanical properties and its capability to heal through hydrogen bonding motifs.

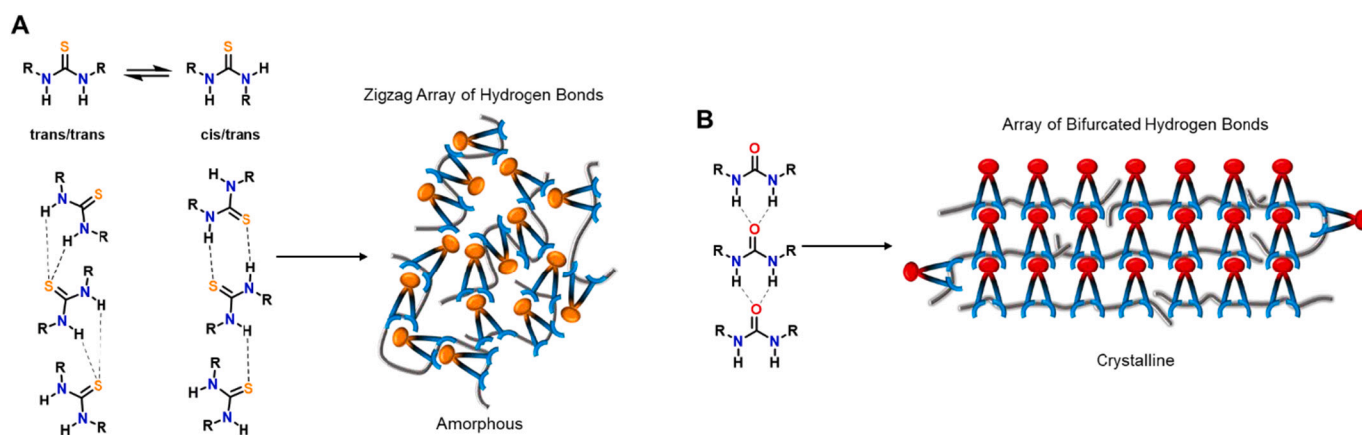


Fig. 14. Schematic representation of the assembly modes of A) thioureas and B) ureas [124].

assembled with varying ratios of $\text{Zn}(\text{NTf}_2)_2$ or $\text{La}(\text{NTf}_2)_3$. Through electron microscopy and small-angle X-ray scattering experiments, the metallosupramolecular polymer exhibited a microphase separated morphology. The poly(ethylene-co-butylene) core formed the "soft" phase, and the metal-ligand complexes formed the "hard" phases. The microphase separated morphology and noncovalent metal-ligand complexes responsible for network formation afforded the material interesting mechanical properties, elongation, and stress at a break of 60–85% and 15–45 MPa. Another metallosupramolecular healable polymer system has been reported by Zhang and co-workers [111]. A dual network was described where Fe^{3+} ions are exploited through metal-ligand interactions and ionic coordination chemistry to impart stiffness and healing to a siloxane network (Fig. 15). The siloxane polymer backbone contained *N*-acetyl-L-cysteine to permit ionic interactions, while 2,6-pyridinedicarboxamide was introduced as a chain extender and served as the ligand. By tuning the assembly motif content, control over mechanical properties and the ability to heal at room temperature was demonstrated.

The integration of metal-ligand interactions in a PDMS network by Bao and co-workers showed an increase in the material's dielectric constant compared to PDMS [138]. In this study, bipyridine is inserted within the PDMS chain to introduce metal-ligand supramolecular cross-linking by Zn^{2+} and Fe^{3+} cations, enabling the material to heal at room temperature and regain up to 76% of its original strain at break over two days. This design strategy shows promise in stretchable electronics based on its improved dielectric constant and reasonable self-healing properties (Fig. 16). Interestingly, by taking advantage of a similar interaction between zinc and urea moieties, a polymer material capable of self-healing at subzero temperature (-20°C) has also been reported [139]. The ability to heal at subzero temperatures offers value where there is an anti-icing coating demand, such as on the leading edges of aeroplane wings and wind turbine blades, potentially increasing these precision pieces' life span reducing the costs associated with their maintenance.

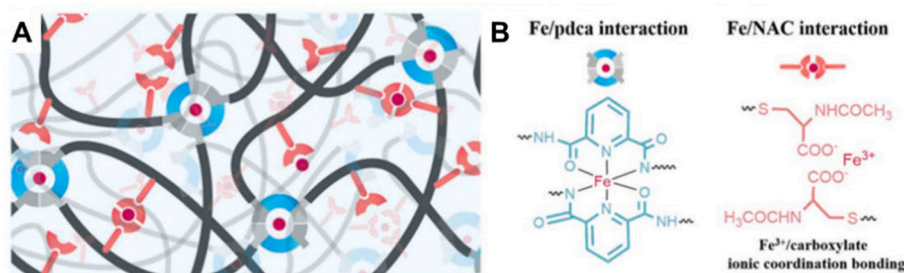


Fig. 15. A) Schematic and B) chemical representation of the dual network interaction in the system. Image reprinted with permission from reference [111].

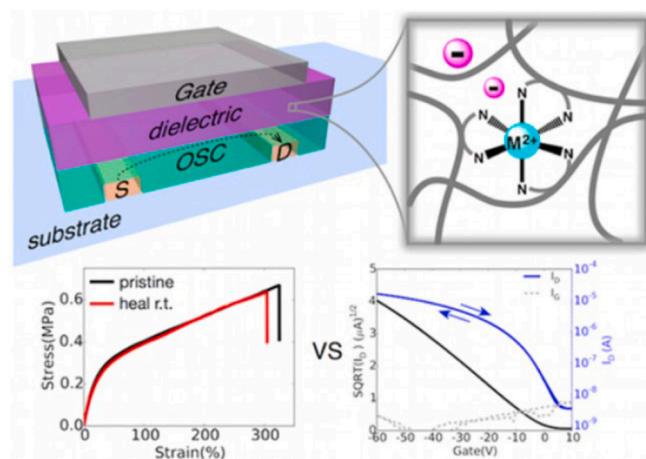


Fig. 16. Schematic representation of the organic field-effect transistors device in a top-gate bottom-contact geometry on the rigid substrate (silicon wafer). Graphs show the mechanical properties and the transfer (I_D versus V_G) and output curve characteristics of organic field-effect transistors with a channel width of $4000\ \mu\text{m}$ (arrows denote gate bias sweep directions and the gate voltage scan rate is normalised to that of $1\ \mu\text{m}$ thickness). Image reprinted with permission from reference [138].

2.4.3. Healable supramolecular polymers that utilise host-guest interactions

Another approach to afford healable supramolecular materials is to employ host-guest interactions as the key network assembly element. Guest elements of molecules/polymers are bound inside the host moieties of a complementary polymer (these are typically macrocyclic receptors) to form a network via the creation of multiple inclusion complexes. Exposure to certain stimuli such as changes in pH, temperature, or oxidation state [140] can reversibly dissociate these

noncovalent host-guest complexes. A wide variety of macrocyclic receptors have been reported in the literature as the host species in host-guest polymeric systems, including pillar[n]arenes [141,142], cucurbit [n]uril (CB[n]s), calix[n]arenes, cyclodextrins (CD) and crown ethers [143]. From these options, cucurbit[n]urils, calix[n]arenes, and cyclodextrins have been employed most successfully to date because the ease of functionalisation of these hosts permits coupling to the polymer. In addition, functionalisation can be utilised to tune the host species solubility based on the target application. One of the advantages of the host-guest approach [144,145] is the host's selectivity towards the guest species to permit efficient and selective network formation and allow for rapid and repeatable healing of the noncovalent network.

Harada and co-workers demonstrated the first example of a healable host-guest system by supramolecular cross-linking poly(acrylic acid) bearing 6 β CD and ferrocene [140]. The control over the inclusion complex was achieved by altering the oxidation state of ferrocene. The hydrogel reported was able to heal a cut in 24 hours at room temperature, provided that the ferrocene was in its reduced form so that the 6 β CD units bound it. Since this report, several groups have introduced and utilised different macrocycles to produce healable systems with tailored applications in specific fields or improve these systems' mechanical performance. Furthermore, various healing methods can simultaneously be utilised in a single system to improve the supramolecular network's healing ability. For example, Lu and co-workers reported a healable system that takes advantage of both UPy end group for complementary hydrogen bonding assembly and CD binding with pyrimidone units to generate a network material that can regain >92% of the physical properties of the pristine network within 36 hours [146]. Zhu *et al.* have reported the development of a healable injectable photonic hydrogel using host-guest and hydrogen bonding interactions [147]. Their system consisted of imidazole-decorated colloidal photonic crystal balls (referred to as 'supraballs') embedded within a UV curable gelatine-based hydrogel, as shown in Fig. 17. The continuous hydrogel phase comprises a hydrogen-bonding moiety and CD receptors and imidazole guest functionalities. Therefore, host-guest and hydrogen bonding interactions between the hydrogel backbones and hydrogel/supraballs lead to healing properties (Fig. 17B & C). The wavelength of

the reflected light from the particles and the particles' colour could be adjusted by changing the particles' size (Fig. 17B). Additionally, the reported supraballs are symmetrical to the extent that the viewing angle does not affect the reflective colour, and the colour remains unchanged by changing the viewing angle from 0° to 75°. Therefore, the light reflectance of supraballs within the hydrogel offers an efficient heat-shielding property (up to 17.4 °C when compared to the pure hydrogel in 4 hours of mid-day sun exposure) which can be further developed to produce advanced healable heat-insulating materials (Fig. 17D).

2.5. Shape memory materials featuring supramolecular polymers

Shape memory polymers are a type of stimuli-responsive polymer that can interchangeably switch from a temporarily fixed geometry to a previously programmed geometry upon applying an appropriate external stimulus [148,149]. This previously programmed geometry can be programmed in various ways, most commonly through permanent covalent cross-links and thermal transitions such as the polymer network's glass or melting transition temperature. Supramolecular polymers have been shown to exhibit shape memory effects utilising dynamic bonds, delivering tunability to mechanical properties and self-healing capabilities [150]. Ma and co-workers have developed a self-healing supramolecular bioelastomer capable of rapid shape memory recovery utilising a poly(glycerol sebacate) (PGS) backbone and UPy grafted via the hydroxy in the repeat unit [151]. Utilising UPy as a physical cross-link, the ability of the supramolecular polymer to heal was evaluated. Three temperatures were chosen for healing (37, 55 and 75 °C, respectively), and as anticipated, the healing efficiency increased with prolonged heating (12 hours) and at higher temperatures (75 °C). However, complete recovery of the mechanical properties was not achieved; in the case of the supramolecular polymer containing ~23 wt % UPy-HDI, a healing efficiency of 85% in terms of tensile strength and 60% for strain recovery was achieved when held at 55 °C for 12 hours in comparison to 40% and 25%, respectively, when exposed to the same temperature for only 30 minutes. At higher wt% values of UPy-HDI, similar healing efficiencies were observed, but relatively weak mechanical properties were recovered when exposed to a temperature of 37

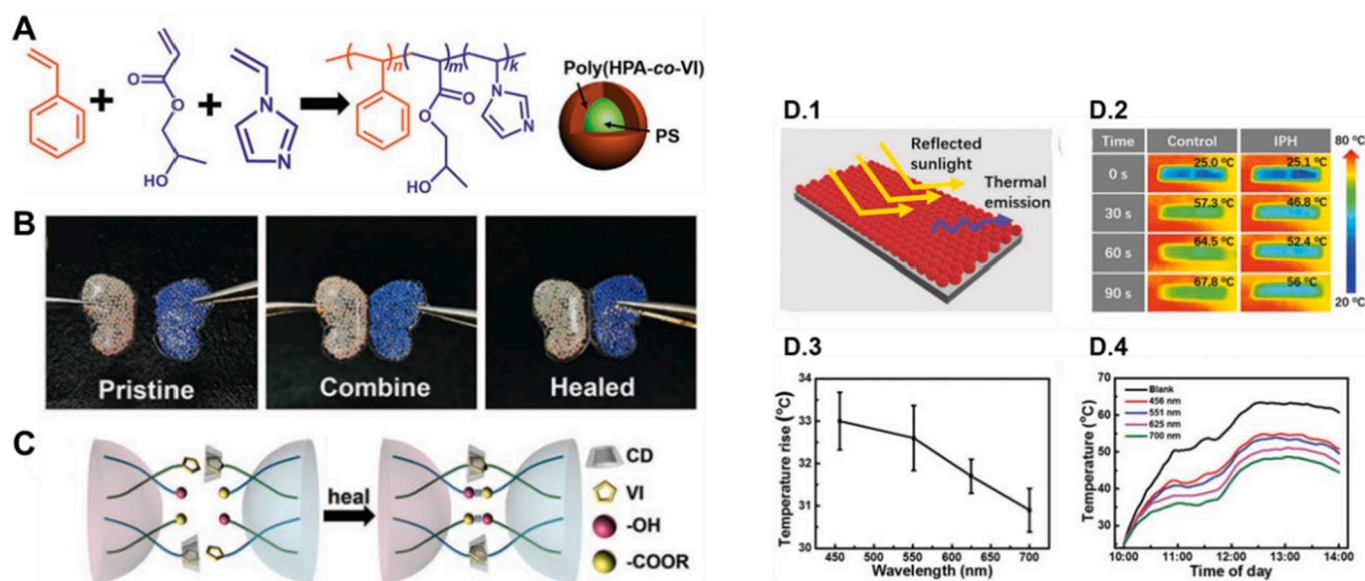


Fig. 17. A) Chemical structure of the functionalised supraballs. B) Two separately prepared parts stick together at ambient temperature after several minutes. The bond is strong enough to allow for the lifting of the attached parts. Additionally, each butterfly half consists of different colours supraballs. C) Healing a freshly cut sample through the reformation of hydrogen bonding and the β -CD/imidazole inclusion complex. D.1) Proposed mechanism of cooling properties of the reported material. D.2) Infrared images of the matrix gel (control) vs the supraball containing gel (IPH) upon sun irradiation for 90 seconds (stopband at ~700 nm). D.3) The effect of stopband position on the thermal insulation properties. D.4) Temperature change of a black sheet in a box covered with glass (black line) or photonic hydrogels with different stopband upon exposure to the midday sun. Image reproduced with permission from reference [147].

°C – healing required exposure to 55 °C and 75 °C for the mechanical properties to be regained effectively.

Similarly, photo-crosslinked metallo-supramolecular polymers have been used to access shape-memory polymers, utilising light, heat, and/or chemicals to disrupt the metal-ligand interactions to recover back to their permanent shape. Rowan and co-workers used a low molecular weight poly(butadiene) end-capped with 4-hydroxy-2,6-bis(10-methylbenzimidazolyl)pyridine (HOMEbip) and subsequently covalently crosslinked with a tetrathiol in the presence of either a Zn or Eu metal salt (Fig. 18) [20]. Metal-ligand complexation acted as the hard phase and, as such, was used to fix a temporary shape. Upon breaking these metal-ligand interactions, the polymer material returned to its permanent shape. The cross-link density of the polymer was also investigated, and it was regardless of the number of cross-links per chain, excellent shape memory properties were observed.

2.6. Use of supramolecular polymers in energy generation and storage devices

Many self-assembled materials possess unique photochemical and electronic properties as a result of the stable nanostructures which they form. Significant effort has been placed on achieving complete control over the relationship between structure and function in polymer electronics, emphasising the role of supramolecular chemistry, which can drive the formation of highly ordered functional assemblies. These unique properties have been utilised to produce novel materials for energy applications and are often integrated into tangible devices. Herein, we highlight several novel and innovative examples of supramolecular polymers in energy generation and storage, however, we direct the reader to excellent review articles [152–154] which explore these areas in greater depth.

2.6.1. Photovoltaic devices featuring supramolecular polymer components

Supramolecular polymers have been utilised to develop photovoltaic devices. Sary *et al.* have reported [155] photovoltaic devices comprised of a thin film nanostructure which was formed by the self-assembly of poly(3-hexylthiophene)-block-poly(4-vinylpyridine) block-copolymers,

forming regio-regular rod/coil-like structures when blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester. The resulting, strong, π - π stacking interactions were able to stabilise the nanostructures in the presence of the fullerenes, which preferentially accumulated within the coil domains resulting in hole transport. Additionally, the poly(4-vinylpyridine) coil demonstrated a new method of accessing electron acceptor domains within the self-assembled nanostructure. When combined with the rod forming and electron-donating poly(3-hexylthiophene) block, a bicontinuous interpenetrating donor/acceptor network was afforded. Interestingly, the block copolymer/fullerene blends were less affected by fullerene crystallisation than fullerene-grafted block copolymers. Blends were shown to be highly soluble in common solvents allowing for ease of processing and the resulting films demonstrated heightened stability, being thermally stable for more than 24 hours at 150 °C when compared to a control bulk heterojunction polymer blend (Fig. 19).

The blends were shown to preserve structural morphologies and hole/electron mobilities with photon-to-current conversion efficiencies equivalent to those of polymer heterojunction reference cells, and overall energy conversion efficiencies beyond those reported for photovoltaic cells whose active layer contain a block copolymer as its principal constituent.

Similarly, a supramolecular complex formed in co-crystalline solids between concave polycyclic aromatic hydrocarbons, namely dibenzo-tetrathienocoronene and C₇₀ fullerenes was also reported [156] by Nuckolls and co-workers. The π - π stacked complexes, which give rise to a ball-and-socket structure with an association constant of 10^5 M⁻¹, were processed from solution to create active layers in a solar cell. An optimised photovoltaic device was prepared by spin coating the self-assembled material with PEDOT:PSS on an ITO-coated glass. An aluminium counter electrode was then applied through thermal evaporation onto a titanium oxide (TiO_x) interlayer. The self-organised films provided high open circuit voltages (V_{oc} = 0.91 V) a short-circuit current density (I_{sc}) of 7.25 mA cm⁻², and fill factor of 0.4, so giving rise to modest power conversion efficiencies (η) of up to 2.66% (Fig. 20).

Supramolecular complexes of porphyrin dendrimers with fullerenes have also been reported for photoenergy conversion. Assemblies

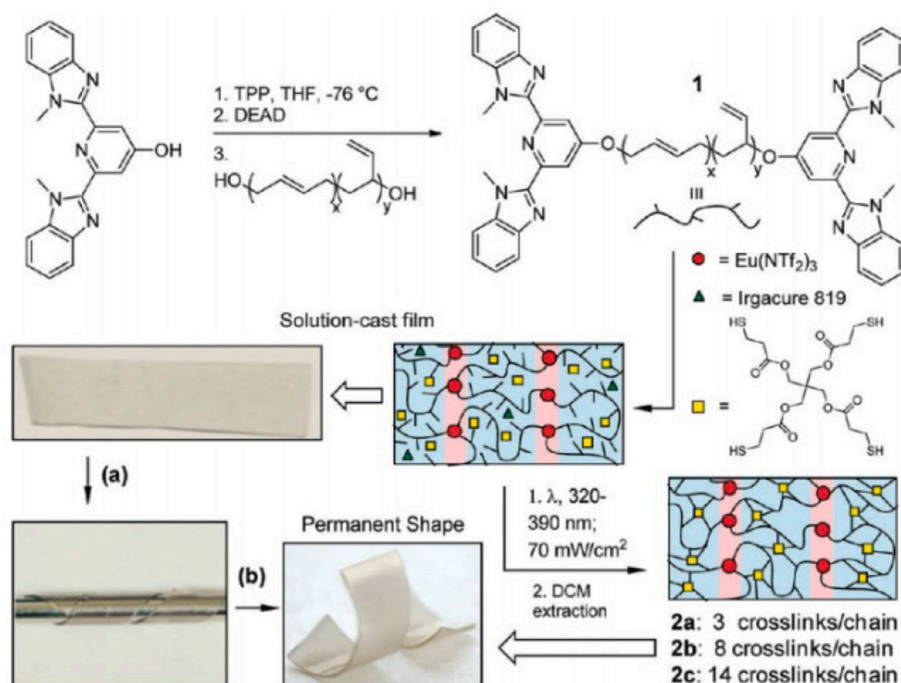


Fig. 18. Reaction schematic and the process of solution casting to subsequently photo-cross-linking with varying amounts of tetrathiol to create films with 3, 8 and 14 cross-links per chain. Fig. reproduced with permission from reference [20].

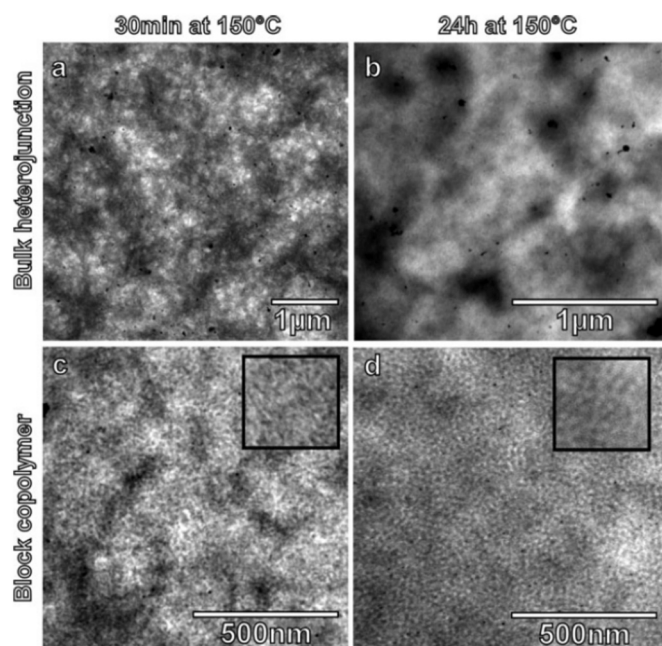


Fig. 19. TEM images of a-b) P3HT:PCBM (1:1) bulk heterojunction control polymer thin films and c-d) P3HT-P4VP:Fullerene block co-polymer thin films after iodine staining and various annealing times at 150 °C. Macrophase separation is observed only in the reference film b, whereas the block copolymer nanostructure improves upon long-term annealing d. Insets show: the nanostructures of the pure block copolymer after 30 minutes c and 24 hours d annealing over a 200 nm × 200 nm surface area. Reproduced with kind permission from reference 155, copyright 2010 John Wiley and Sons.

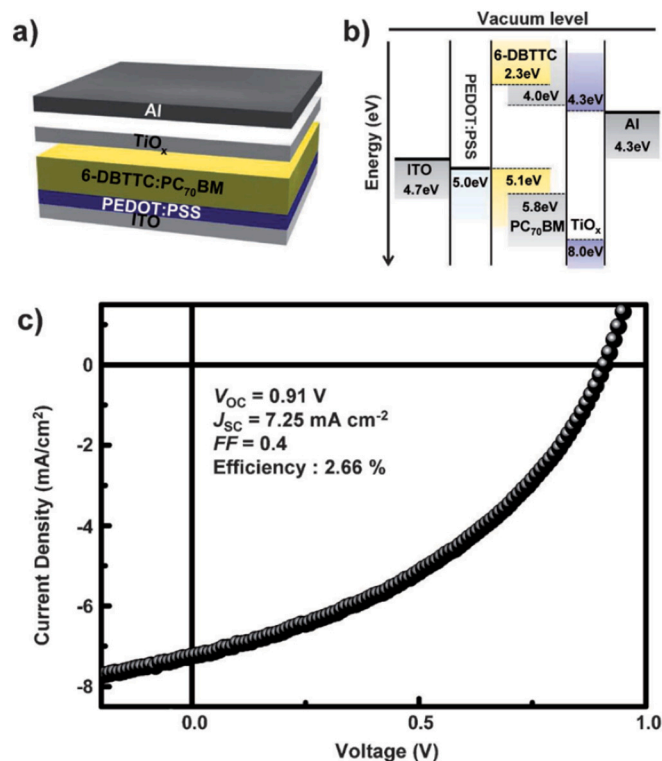


Fig. 20. a) Schematic illustrations of the device architectures of the 6 solar cell. b) Energy level diagram of the device components. c) Current density–voltage (J – V) characteristics of a representative device under light illumination. Reproduced with kind permission from reference 156, copyright 2012 John Wiley and Sons.

formed by cluster formation in a mixed solvent on nanostructured SnO₂ electrodes were reported [157] by Hasobe *et al.* in which molecular assembly gave rise to controlled the three-dimensional molecular structures. The materials afforded an efficient photoresponse in the visible and near-infrared regions, and a high photoenergy conversion efficiency as a result of effective electron transfer from the excited porphyrin to fullerene within the dendritic matrix. A fill factor of 0.31, open circuit voltage (V_{oc}) of 220 mV, short circuit current density (I_{sc}) of 0.29 mA cm⁻², and an overall power conversion efficiency (η) of 0.32% at an input power (W_{in}) of 6.2 mW cm⁻² was recorded, demonstrating the possible use of dendrimers in solar cells.

2.6.2. Deployment of supramolecular polymers in battery technologies

Another use of supramolecular polymers for energy applications is their deployment in batteries. Organic cathode materials are promising candidates for a new generation of green batteries, since they have low toxicity and can be produced from renewable resources. Deng and co-workers have built on the studies [16,125] of Meijer and Sijbesma by applying their quadruple hydrogen bonding motif, ureidopyrimidinone [11], to develop a healable supramolecular comb-polymer binder for high-performance silicone anodes for lithium ion batteries [158]. Silicone undergoes significant volume changes during charge and discharge cycles leading to loss of capacity and reduced life cycles. The healable polymer network comprising of poly(acrylic acid) and ureidopyrimidinone (PAA-UPy) exhibited strong binding between the silicon particles and itself. Furthermore, it was shown to effectively withstand the large volume change of the silicon anode upon lithiation and delithiation (Fig. 21) through the reorganisation of the polymer network.

The electrochemical properties of the PAA-UPy polymer binder were extensively explored (Fig. 22). An initial discharge capacity of 4194 mAh g⁻¹ measured at a current density of 210 mA g⁻¹ was achieved from the composite, whilst a relatively high capacity of 2638 mAh g⁻¹ was achieved after 110 cycles, revealing the good long-term cycling stability. A favourable Columbic efficiency of 86.4% was superior to Si anodes using poly(acrylic acid), carboxymethyl cellulose, and polyvinylidene difluoride as binders. Furthermore, the anode with the dynamic polymer matrix showed the highest reversible capacity (3592 mAh g⁻¹) of all materials explored. As a consequence of the reversible characteristics of the anode's polymer matrix, a capacity retention of 2662 mAh g⁻¹ was achieved, even at a high current densities. This gave rise to excellent rate performance when compared to the control materials with only a small impedance increase. The substantial enhancement in electrochemical performance of the PAA-UPy was attributed to the supramolecular network formed and the dynamic nature of the polymer matrix. It was proposed that the self-assembly of the polymer matrix may enable the development of stable silicone electrodes which high capacities and long-life cycles for use in commercial lithium-ion batteries [158].

A similar concept was also employed [159] by Kwon *et al.* in which a host-guest system containing β -cyclodextrin recognition motifs on a polymer backbone blended with dendritic gallic acid cross-linkers containing adamantane were prepared for high-capacity silicon anodes (Fig. 23). The dynamic network allowed for intimate and spontaneous interactions between complementary motifs, with an association constant in the order of 10⁴ M⁻¹, giving rise to a structurally stable electrode gel. Furthermore, the polymeric network afforded possessed adhesive capabilities to silicone anodes. Predictably, the polymer was able to self-heal and could be used to restore broken electrode contacts during the volume changes experienced during charge and discharge. Furthermore, galvanostatic measurements with Li half-cells were performed to understand the effect of host-guest interactions on the electrochemical performance of silicon anodes. Highest capacity retention (90% after 150 cycles) was found in a 1:05 (CD:AD) stoichiometry, which was a significant improvement on conventional linear binders which only achieved 30.5% after 150 cycles. Finally, SEM analysis was used to inspect the morphology of the silicon nanoparticles coated with

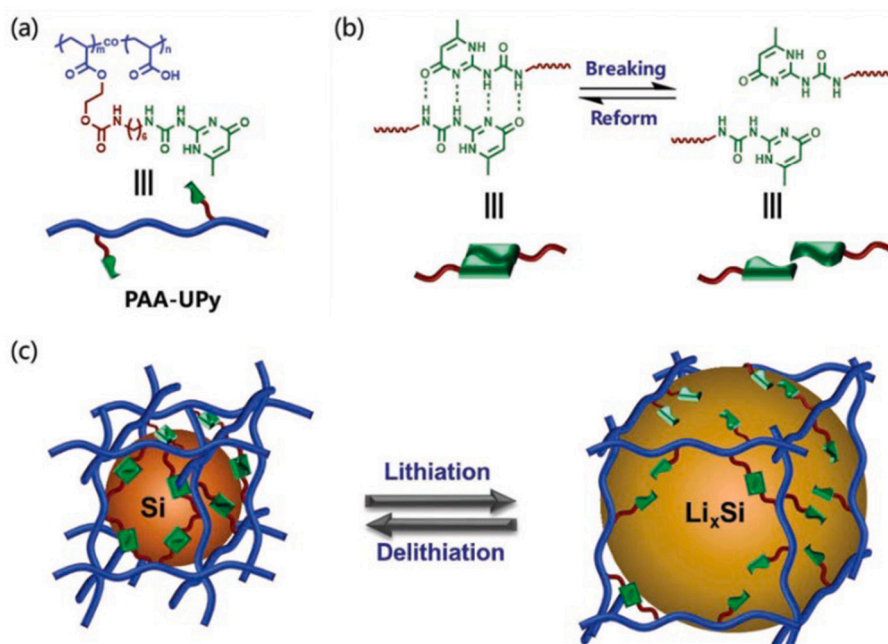


Fig. 21. a) Structure of the poly(acrylic acid)-UPy co-polymer, b) the reversible interactions between UPy dimers, and c) schematic of the charge–discharge process of silicon anodes using UPy polymer binder. Adapted with kind permission from reference 158, copyright 2018 John Wiley and Sons.

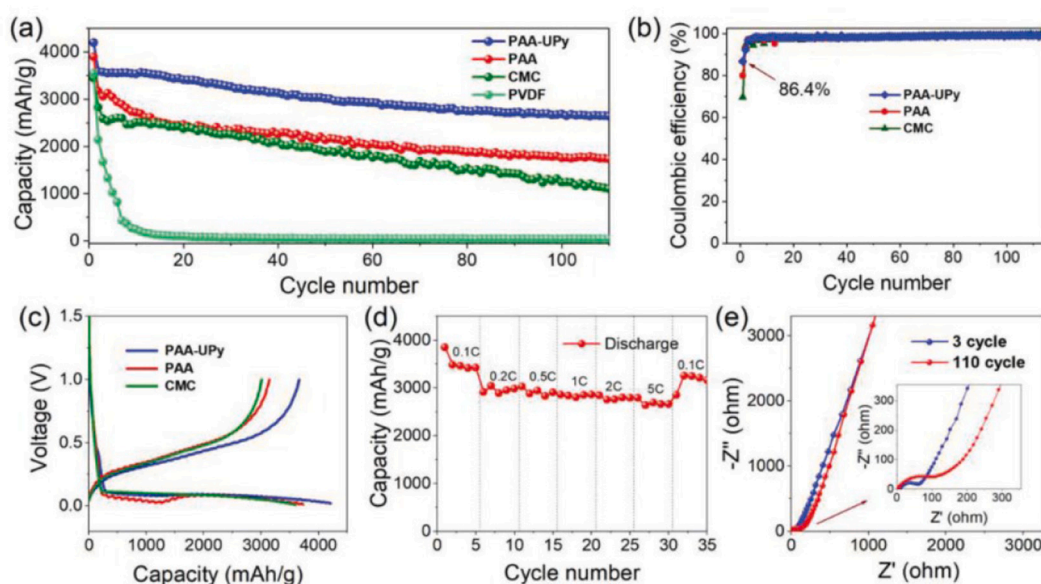


Fig. 22. Electrical properties of the healable polymer network (PAA-UPy) compared to reference polymers, showing a) the cycling capacity of the silicon electrodes employing b) Coulombic efficiencies c) the charge-discharge profiles of electrodes after the first cycle d) rate retention of the Si electrode and e) Nyquist plot at varying number of cycles showed a small impedance increase. Reproduced with kind permission from reference 158, copyright 2018 John Wiley and Sons.

β -cyclodextrin containing polymers. Even after 150 cycles, the material maintained well-defined morphologies without any micro-cracks, suggesting that the dynamic cross-linking enabled stability throughout the large volume changes experienced in multiple charge and discharge cycles.

2.6.3. Capacitor devices featuring supramolecular polymers

An alternative method of storing energy in capacitors and supramolecular polymers have been employed to advance these devices. In 2016, Guo *et al.* fabricated [160] a ferric ion (KCl-Fe^{3+}) cross-linked supramolecular poly(acetic acid) cross-linked hydrogel electrolyte for use in

flexible supercapacitors (Fig. 24). By modifying the ion concentration, and thus the supramolecular cross-link density [18,161], the mechanically robust polymeric gelator could be tuned to yield high elasticity (> 700%) or greater strength (ultimate tensile strength > 400 kPa). The electrochemical performance of the supramolecular polymer was assessed by assembling with a graphene foam containing pyrrole monomer as electrodes. The device recorded a specific capacitance of 87.4 F g^{-1} at a current density of 0.5 A g^{-1} in dual electrode systems and 349.6 F g^{-1} in a single electrode system. After 5000 charging–discharging cycles, the capacitance retention rate was shown to reach 89% at a current density of 1 A g^{-1} , demonstrating good versatility of the flexible

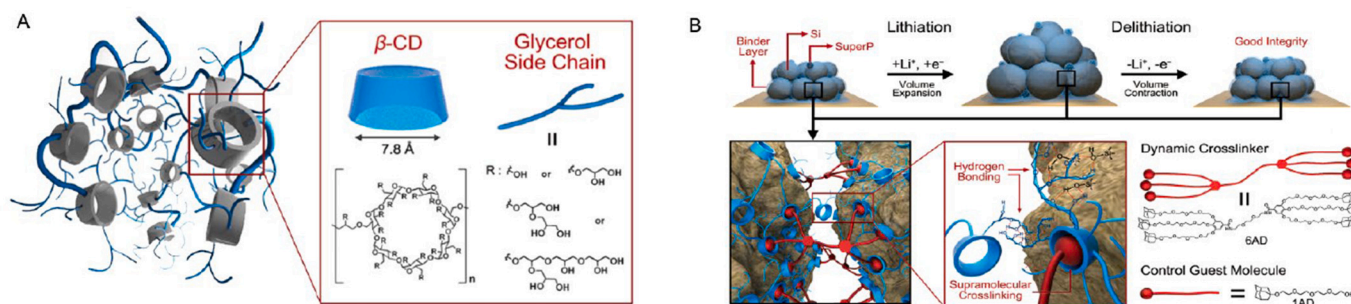


Fig. 23. A) Graphical representation and chemical structures of hyperbranched β -CD polymer. B) Proposed working mechanism of dynamic cross-linking of β -CD and 6AD in an electrode matrix along with graphical representations and chemical structures of guest molecules incorporating adamantane moieties. Adapted with kind permission from reference 159, copyright 2015 American Chemical Society.

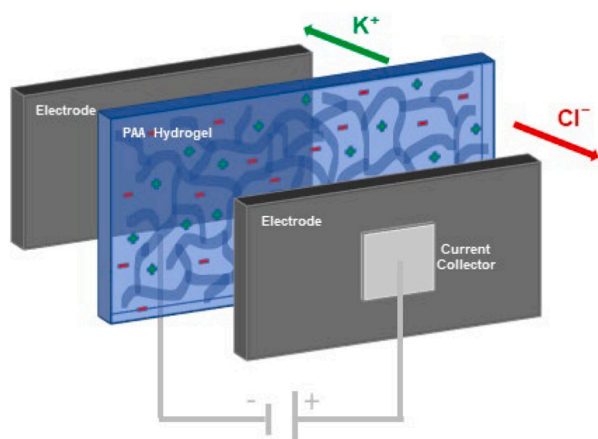


Fig. 24. Design of the KCl-Fe^{3+} /PAA hydrogel showing ion transport [160].

hydrogel. Interestingly, conductivity was shown to be independent of cross-linking ferric ion concentration with a conductivity of 0.045 S cm^{-1} reported at a swelling ratio of 150%. The conductivity of the gel could be further increased to 0.09 S cm^{-1} by accessing higher rates of swelling (300%). Finally, the non-covalently cross-linked hydrogelator demonstrated healing ability when damaged and subsequently brought into close contact at room temperature for 24 hours with apparent healing efficiencies close to 100%. Furthermore, the polymer was able to undergo facile reprocessing through dissolution before being fabricated once again into a film.

Hydrogel polymer electrolytes that have found use in electrochemical double layer capacitors as a result of their ability to avoid electrolyte leakage risk, often suffer from narrow electrochemical

windows. To address this Li *et al.* have developed [162] a deep eutectic solvent-based supramolecular polymer gel electrolytes composed of urea, LiClO_4 , polyvinyl alcohol, and glycerol. Carbon-based electrochemical double-layer capacitors were assembled by sandwiching the supramolecular polymer gel between two electrodes and the electrical properties examined (Fig. 25). The device was able to access a wide operating cell voltage range of 2.4 V, offering improvements over aqueous based analogues. Furthermore, a specific capacity of 31.1 F g^{-1} and high energy densities of 24.6 Wh kg^{-1} were achieved, which suggested the material offered a viable alternative for capacitor materials. When the system was further modified with quinhydrone, the energy density of the corresponding capacitor was further increased to 43.6 Wh kg^{-1} . Furthermore, nearly 90% of its initial capacitance was retained after 15,000 charge-discharge cycles revealing excellent cycling stability and the potential of these materials in capacitor applications.

2.6.4. Application of supramolecular polymers in semiconductor technologies

Another vibrant area of research in which supramolecular polymers have found application in energy materials is semiconductors. Fréchet and co-workers have prepared [163] an easily processable semiconductor by molecular design of modular oligomers that can self-assemble with a comb-polymer to form well defined coil-comb arrays. A quaterthiophene organic semiconductor was installed on the side chains of poly(styrene)-*block*-poly(4-vinylpyridine) via hydrogen bonding interactions (Fig. 26) to form p-type semiconductors in a field-effect transistor which was able to be readily processed from solution. The hierarchical assemblies formed by the macroscopic alignment of the organic semiconductor thin films gave rise to channels that could transport charge. DSC experiments revealed that the hydrogen bonding interaction between the two moieties was unstable at $110 \text{ }^\circ\text{C}$, and remained present up to $190 \text{ }^\circ\text{C}$. The melting temperature of the supramolecular assembly was within the temperature regime required to

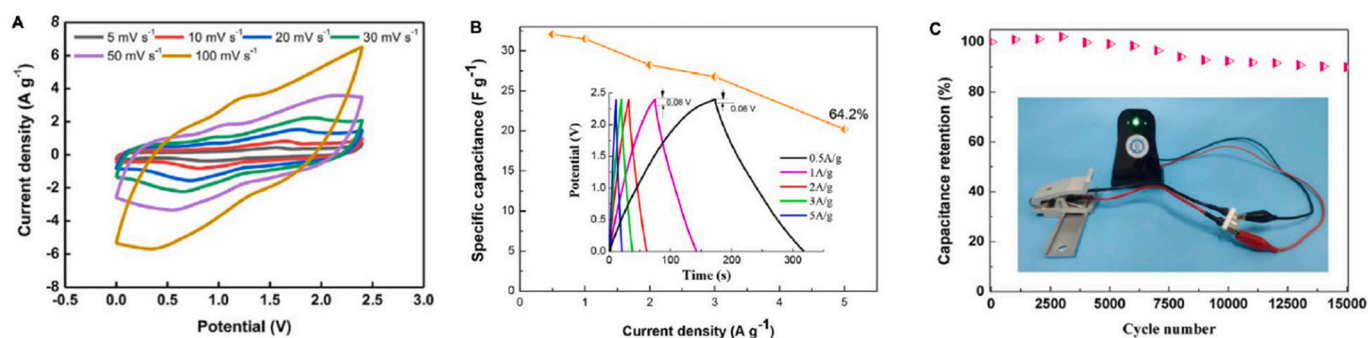


Fig. 25. A) CV curves of the quinhydrone doped electrochemical double-layer capacitor at different scan rates. B) Variation of specific capacitance with current densities of the electrochemical double-layer capacitors. Insert: Galvanostatic charge-discharge curves at different current densities. C) Cycling performance of the capacitor at 5 A g^{-1} . Insert: Green LED powered by the capacitor reported. Adapted with kind permission from reference 162, copyright 2021 Elsevier.

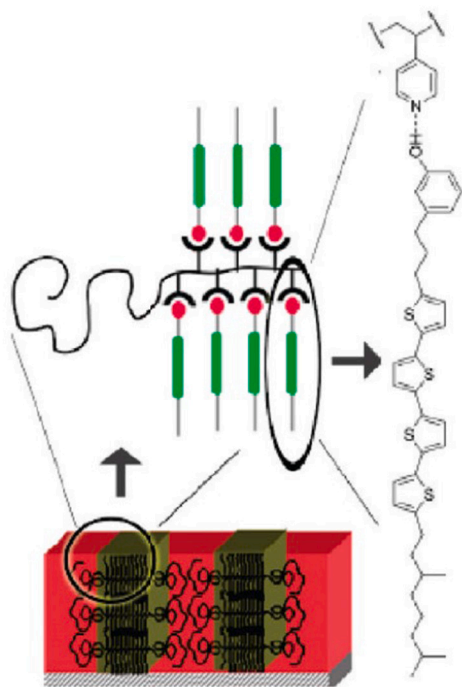


Fig. 26. Representation of the ideal hierarchical assembly of PS-b-P4VP in thin films for OPV fabrication, where BCP microdomains are oriented normal to the surface. Adapted with kind permission from reference 163, copyright 2010 American Chemical Society.

access the amorphous state without destroying the non-covalent interactions. A top-contact, bottom gate OFET device was prepared and the charge transporting capabilities explored. Films were annealed at 110 °C for 10 minutes after spin-coating onto silicon wafers to give rise to uniform films. The morphology of the polymer films was explored using SAXS and TEM which revealed hierarchical assemblies that may satisfy many morphological requirements for high-efficiency OPVs. Mixed morphologies were observed for supramolecules annealed at 110 °C, and lamellae-within-lamellae morphology was observed after thermal annealing at 155 °C. Charge mobilities of 10^{-4} $\text{cm}^2/(\text{V}\cdot\text{s})$ were recorded for the supramolecular polymer when solvent-annealed in chloroform vapours. Low off-currents suggest that a low level of doping was present in the polymer films, whilst low turn-on voltage suggested a low barrier to mobile charge injection. Indeed, on/off ratio of 10^3 were recorded for the devices. The top-contact, bottom-gated OFET experiments demonstrated the functionality of the supramolecular film assemblies in energy materials.

A novel donor-acceptor type copolymer, poly(didodecylquaterthiophene-*alt*-didodecylbithiazole), was prepared [164] by Kim *et al.* that contained electronically complementary electron-donating quaterthiophene and electron-accepting 5,5'-bithiazole units to form semiconductors. Electronically active liquid-crystalline polymer semiconductors were prepared by annealing at 180 °C which resulted in highly crystalline thin films with a clear mesophase region that spontaneously formed. AFM investigations of the thin films annealed at the mesophase revealed polycrystalline structures with highly ordered rod-shape grains of 300-500 nm in length, as a consequence of the self-organization of the polymer chains oriented perpendicularly to the substrates in the liquid-crystalline phase. A high ionisation potential value (5.19 eV) when compared to poly(3-hexylthiophene) (P3HT) was reported, suggesting that the resulting bottom-gate top-contact OFETs were likely to have a low off-state current (non-oxidative state). Typical output characteristics (I_D - V_D) at different gate voltages of OFETs were consistent with p-type semiconductors, showing well-resolved current linear regimes (ohmic region) in the low drain-source voltage range (V_{DS}

< -1 V) and a saturation current near 16 μA at gate voltages of -40 V. Furthermore, no significant hysteresis was observed in the devices. Notably, the π - π stacked copolymer exhibited attractive electrical characteristics, with field-effect mobilities of up to $0.33 \text{ cm}^2\text{V}^{-1}\cdot\text{s}^{-1}$ and good bias-stress stability (measured at -20 V for 3 hours) when compared to amorphous silicon. These materials provided a facile means for fabricating highly ordered semiconductor channel layer with a minimal concentration of charge traps and high electrical stability.

Supramolecular energy materials are wide spanning area of research within materials science with enormous potential to transform the way renewable energy is produced and used, and will help contribute to a sustainable energy future. Critical advancements in energy generation and storage, through understanding of how macromolecular systems interact to create functional systems have been aided by developments in synthetic chemistry and materials science [165–168]. Supramolecular systems will undoubtedly play a crucial role in developing the next generation of materials in this vibrant area of necessary research [152].

2.7. Supramolecular polymer sensor systems

Sensors are becoming increasingly essential devices in the interconnected, smart world that is being built around us: the so-call *Internet of Things* [169]. Their aim is to remove the labour-intensive human observations which are still frequently required to monitor parameters as diverse as temperature, pressure or concentrations of specific chemicals (chemosensing). Clearly, with respect to chemosensing, a covalent bond forming reaction between the molecule of interest with a sensing residue designed to given a change in a physical parameter (e.g. fluorescence [170]) will result in a useful sensory readout. However, unless the reaction can be readily and automatically reversed, this approach to chemosensing results in a single use sensor. In contrast, as a consequence of the transient nature of supramolecular interactions, any complex formed with an analyte that results in an 'on' sensing readout can be readily reset by expelling the analyte. This shifts the position of the equilibrium of the system back towards the 'off' position, in readiness for further sensing.

With this design protocol for producing polymeric sensors based on supramolecular interactions in mind, the success of a new sensor is primarily dependent on three parameters: i) *sensitivity* – what is the minimum quantity in analyte that can be detected; ii) *selectivity* or *specificity* – the ability of the sensor to respond to the desired analyte without interference from completing variables; iii) *read out* – how easily can the output of the sensor be converted into a form that can be automatically analysed and used to monitor the system. As the field matures and such sensors are seeking to be implemented in real world situations then this latter criterion becomes ever more important. For example, an extremely sensitive detection system that relies on changes in the chemical shift specific nuclei in solution as a consequence of supramolecular complex formation requires a costly and non-portable NMR spectrometer to produce the result. It is, therefore, unlikely to be suitable for most 'field work' based analysis problems.

This section of the review seeks to exemplify the field polymer sensors that work by supramolecular interactions with an analyte using select examples from the literature that focus on the detection of explosives [171], chirality [172] and physical properties such as strain or damage [173].

2.7.1. Detection of explosives

The group of Swager has pioneered the use of poly(arylene ethynylene)s [174] (Fig. 27A) for the detection of explosive molecules including trinitrotoluene (TNT) and close structural analogues such as dinitro toluene (DNT) (Fig. 27B) [175]. It was observed that films cast from these polymers underwent fluorescence quenching when exposed to vapours of these nitro-compounds as a consequence of electron transfer between the relatively π -electron rich polymers and π -electron poor analytes. The degree of quenching (sensitivity) was dependent on

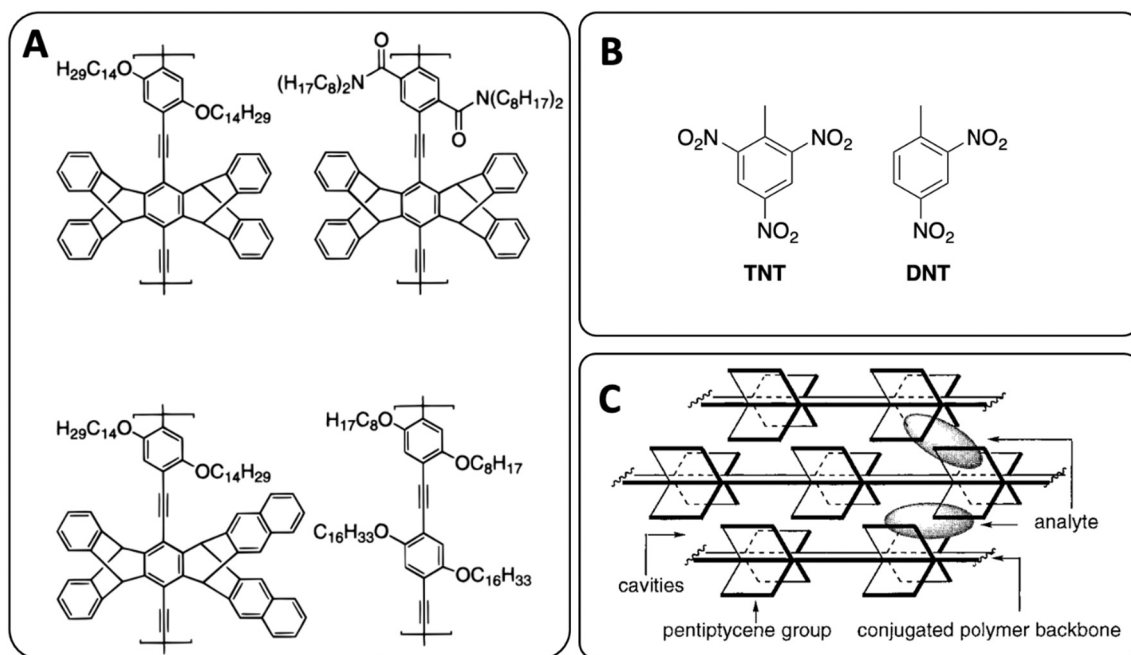


Fig. 27. (A) Chemical structure of the poly(arylene ethynylene)s (PAEs) produced by Swager et al. (B) Structures of TNT and DNT analytes. (C) Proposed position on the p-electron deficient analytes within the solid-state structure of the of PAEs. (Adapted with permission from [175]).

several competing factors, for example, vapour pressure, the binding between the analyte and the polymer and the diffusion of the analyte into the polymer. The polymers containing pentiptycene residues along the backbone exhibited a significant enhancement in sensitivity when compared to the polymer that contained only straight chain octanol substituents (Fig. 27A). It was proposed that the increased sensitivity arose from the ability of the analytes to diffuse more readily into the more porous films. Significantly, studies conducted by the Swager group demonstrated that the polymeric sensors are significantly more sensitive than small molecule analogues of the receptor sites. This can be accounted for by considering that a single analyte polymer interaction results in the fluorescence quenching of either one entire polymer or multiple polymer chains (Fig. 27C), rather than of a single monomer unit.

2.7.2. Detection of chiral molecules

Fukuhara and Inoue have designed elegant systems to sense chirality using supramolecular interactions between chiral molecules and polymers [176]. In this system an enantiomeric binaphthyl crown-ether unit

was connected to the adjacent residues on the backbone of a fluorescent polythiophene (see BTP in Fig. 28). In the uncomplexed state, the thiophenes adopted an anti-conformation. However, upon adding a suitable chiral guest molecule (e.g. D-Ala-OMe.HCl) to the polymer, small but measurable hypochromic and hyperchromic shifts were observed in the CD spectrum at approximately 350 and 450 nm, respectively. This was attributed to complexation between the guest species and the chiral crown ether derivative which caused a re-orientation in the mainchain of the polymer from a planar anti confirmation to the twisted confirmation where the thiophenes are positioned syn with respect to each other.

2.7.3. Strain and damage sensing using supramolecular polymers

In 2018, Weder and co-workers produced a polyurethane-based material that reversibly changes colour in response to an applied force (Fig. 29A) [177]. The linear polymer contained a diol monomer unit comprised of a rotaxane mechanophore (Fig. 29B). The mechanophore contained a fluorophore containing macrocycle interlocked with an electronically complementary quenching residue (NDI). In the relaxed

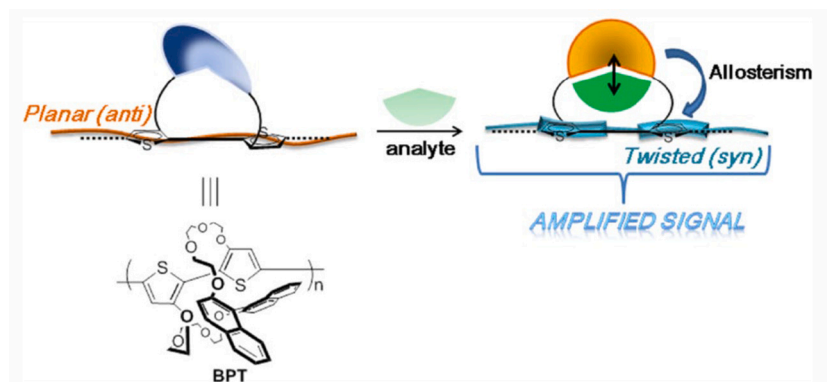


Fig. 28. Schematic of the sensing of chiral molecules by the interaction of the analyte with a crown-ether like receptor on a fluorescent polymer backbone. On complexation the conformation of the thiophene residues on the backbone shift from a planar (anti) orientation to a twisted (syn) alignment. Fig. reproduced with permission from [176].

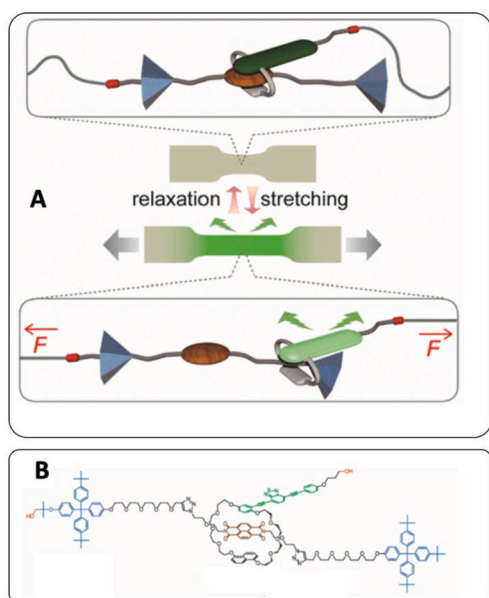


Fig. 29. (A) Schematic of the force-sensing PU synthesised by Weder and co-workers focussing on the rotaxane component, showing the displacement of the macrocycle from its equilibrium position under applied force. (B) chemical structure of the rotaxane monomer used to synthesise the force sensitive PU. (Adapted with permission from [177]).

(force off) state, the system is non-fluorescence as the macrocycle is positioned over the NDI. However, when force is applied, the macrocycle is spatially separated from the NDI, resulting in emission from the system. Removal of the force returned the system to the non-fluorescent

starting state.

2.8. Molecular motors and supramolecular polymer machines

The discovery of molecular machines began with fundamental studies of the self-assembly of relatively simple molecules, and since these seminal studies on host-guest complexes, this field has progressed towards the realisation of ever more complex molecular systems. The synthesis of the first mechanically interlocked catenane was reported [178] by Sauvage in 1983, and in 1991, Stoddart and co-workers described the development of the first molecular rotaxane "shuttle" [179]. These studies on mechanically interlocked catenanes and rotaxane work proved to be the foundation of molecular machines in the Stoddart laboratories whereby temperature-responsive mechanical switching of a π -electron-deficient bipyridinium cyclophane "shuttle" along a polyether "thread" featuring two π -electron-rich hydroquinone units as "stations". This field's importance, potential value, and progression was recognised in 2016 when the chemistry Nobel Prize was awarded to Feringa, Sauvage and Stoddart "for the design and synthesis of molecular machines" [180–182]. These artificial minute machines aim to mimic natural nanomachines' function, such as proteins, in which nanoscale movements result in an operation/task. These nanoscale movements are performed as a response to appropriate chemo-, electro-, or photonic stimulus.

More complex molecular machines have since been synthesised, which are capable of performing various movement depending on their specific design; these include 1) bistable and track molecules (molecular shuttles) [183–188], 2) rotating molecules (molecular motors) [189–194] and 3) scissor-like molecules [195,196]; supramolecular interactions are mainly adopted in the synthesis of the first category (Fig. 30). Although the concept of molecular machines and motors is still considered in its infancy, fundamental research [197–199] is ongoing to

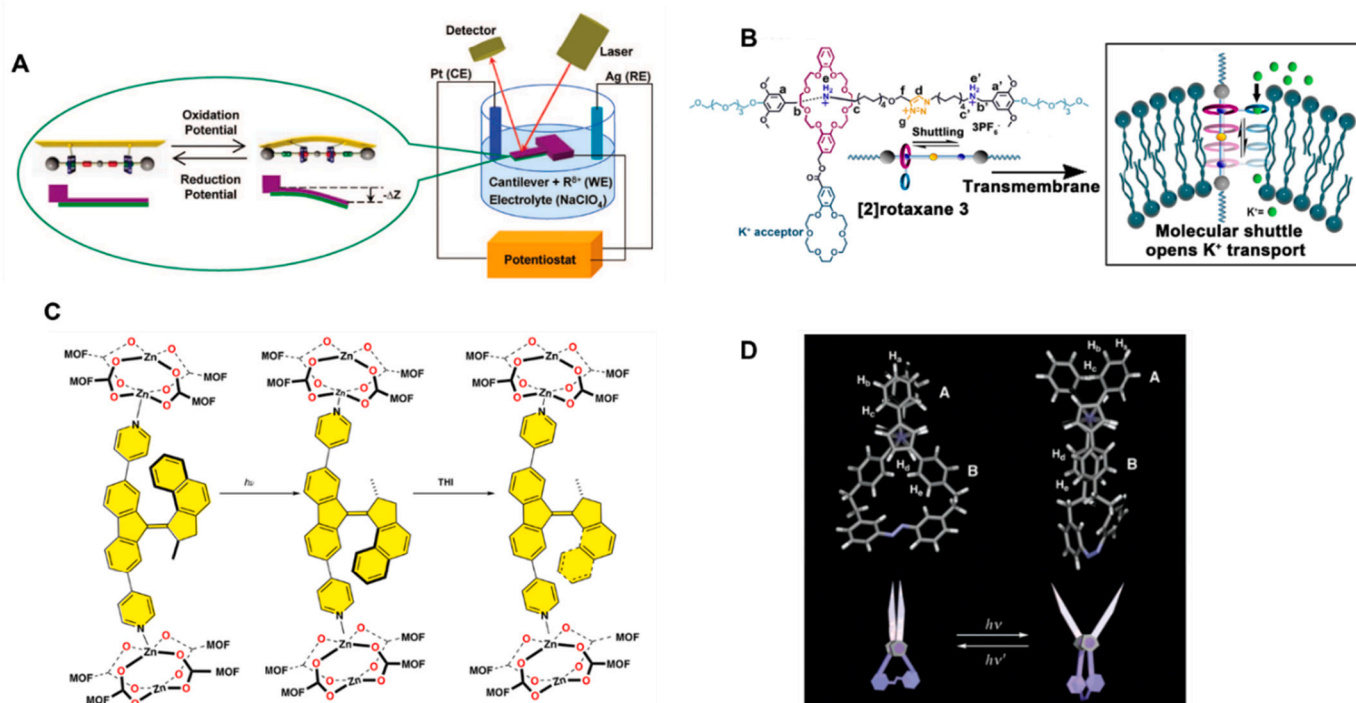


Fig. 30. Examples of different molecular machines based on their class of movement. A and B are supramolecular track/shuttle. A) the material reversibly deflects upon repulsing the CBPQT4⁺ rings by the oxidised tetrathiafulvalene stations. B) The amphiphilic [2]rotaxane works as an ion transfer between lipid bilayers. The [2] rotaxane macrocycle tethers an ion carrier, and by altering the pH, it transfers the ion to the subsequent lipid layer. C) a unidirectional molecular motor based on over-crowded alkene is incorporated into zinc-based MOF as a foundation to build molecular machines with established 3D structures. D) In this scissor-like structure, ferrocene acts as the anchor, azobenzene is the handles, and two phenyl groups are the blades. Photoisomerisation of the azobenzene results in the opening and closure of the scissors. (Images reproduced with permission from references [184, 187, 191, 195]).

fully understand the mechanism of their switching behaviour motion and adapt these chemistries for applications of commercial value.

Any molecular machine must bring significant advancement to its field of use when compared to the current commercially available solutions, and thus careful design plus efficient syntheses of these switchable molecular machines is required. For instance, several groups have explored supramolecular molecular machines to date to mimic membrane transport proteins [200,201]. These proteins can carry a specific ion inside and out of a cell by passing through the lipid membrane. Currently, the artificial transmembrane transferring of ions is carried by employing either channel [202] or carrier (transporter) [203] technology. Channels are tunnels created within the membrane to allow for the movement of ions. These channels are relatively big cavities that allow for dual-way movement of the ions driven by the ion gradient concentration with minimal selectivity. Molecular machines could be considered a progression towards enabling selective and efficient ion transfer carriers. A variety of molecular motions have been proposed enabling the transport of ions, including molecular shuttle [187] and swings [204]. Zeng and co-workers illustrated the process of a transmembrane ion transfer using a molecular swing [204]. A combination of 15-crown-5 and 18-crown-6 units were used as the swing seat responsible for carrying ions. The cyclic molecular seat forms a complex with the ion, and with a swing movement, it transports the ion through the lipid membrane and releases it inside the cell (Fig. 31). By exploiting fluorescence dye indicators and introducing gradient ion concentration extra/intravesicular, this molecular swing functionality has been studied and proved most effective in carrying K^+ ions across membranes. In patients with glioblastoma, the extravascular concentration of K^+ ions around the tumour is high, which results in the malfunction of the neighbouring neurons. The reported molecular swing has thus been studied in the glioblastoma cell line as a possible cancer chemotherapy treatment, and its IC_{50} was found to be lower or equal to the current therapies, which indicate significant anti-cancer efficiency.

Another widely explored class of supramolecular machines is molecular muscles. The compilation of the molecular level motions is converted into a mechanical macroscale movement to perform a specific task [205]. The concept of these artificial molecules is inspired by biological molecules such as myosin that perform mechanical work by consuming the energy provided by adenosine triphosphate (ATP), the cells chemical fuel [206]. Many of these molecular muscles are synthesised utilising a so-called 'daisy chain' molecular strategy. Daisy chain molecules are made up of interconnected inclusion complexes in which

each ring is covalently connected to a thread encircled by the ring of the adjacent thread. The ring of the neighbouring "daisy" can move along the thread, where the inclusion complex is formed, the movement which leads to the overall length change. For example, Harada and co-workers synthesised a [C2] daisy chain hydrogel exploiting the inclusion complex between cyclodextrin and *trans*-azobenzene [207]. Upon irradiation of UV light (365 nm), the hydrogels molecular contraction and the corresponding xerogel produce ca. 0.12 μ J work by bending towards the irradiation source. The rate of this shape change is 10600 times higher in the xerogel form. It was also demonstrated that the reported xerogel is mechanically robust enough to pinch and hold a 107.8 mg matchstick with the aid of an iron plate (Fig. 32), which can be used as a molecular robotic arm. Although irradiation of visible light (430 nm) proved effective in extending the bent hydrogel back to its original shape, a macro-scale shape change was not observed in the xerogel. The isomerisation of azobenzene is reversible in both hydrogel and xerogel; the cyclodextrin rings cannot move and reassemble with *trans*-azobenzene in xerogel because of lack of hydrophilic interactions in the dry state. The xerogel was forced back to its original shape by a second exposure of UV irradiation from the opposite side to perform a *pseudo*-reversible task.

2.9. Biomedical devices and therapies featuring supramolecular polymers

Supramolecular polymers have been studied extensively in the development of biomedical devices and therapies. The versatility and their tuneable physical and mechanical properties resulted in the development of materials for intracellular protein delivery [208], bone regeneration scaffolds [99] and to facilitate prosthesis adhesion [209] or the delivery of drugs that are unstable or prone to rapid excretion [208,210,211].

Nanotherapy approaches utilising supramolecular polymers for cancer treatment have recently received attention from several groups [212,213]. Therapeutic nanoparticles have been approved for use and are now used to treat cancer patients [214]. Nanoparticles can serve as efficient drug carriers and reach the cancerous site through blood circulation to offer a targeted drug delivery to the tumour site, thus avoiding harm to healthy tissues and overall, this approach reduces the toxicity of the drug to the patient [214,215]. Adaptable supramolecular polymeric nanoparticles and their responsiveness make them an efficient candidate as a drug carrier for localised delivery [212,213,216]. For example, Sun *et al.* have developed double responsive

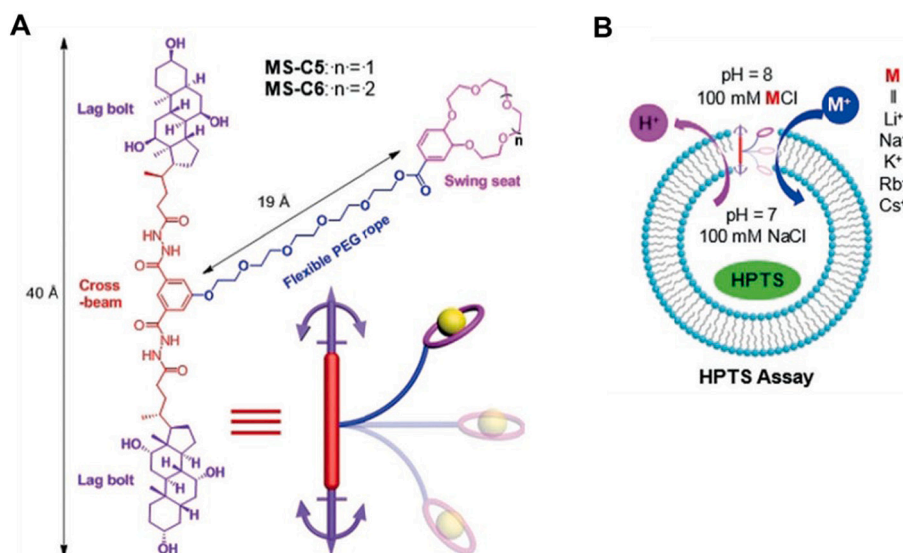


Fig. 31. A) chemical structure of the molecular swing and its graphical representative. B) Schematic of the ion transfer activity in the pH-sensitive HPTS assay. Image reproduced with permission from reference [204].

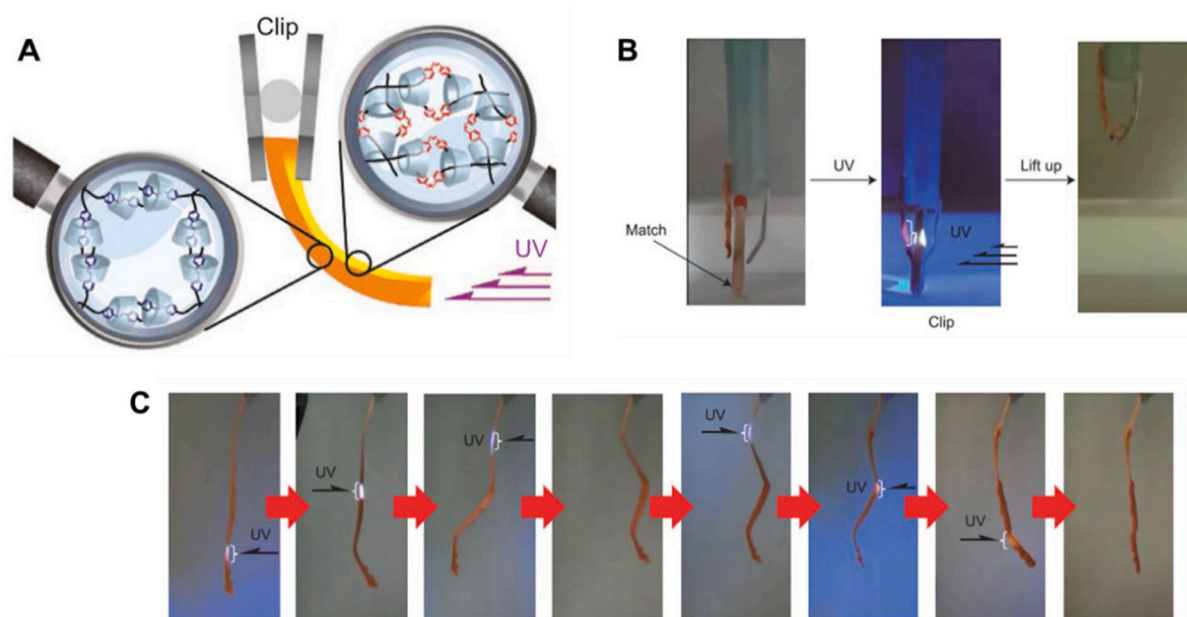


Fig. 32. A) the chemical structure of hydrogel/xerogel molecular muscle performing a task, B) showing the xerogel's ability to pinch and hold a matchstick, and C) the pseudo-reversibility of xerogel movement. Image reproduced with permission from reference [207].

supramolecular nanoparticles for cancer therapy [216]. In this study, Paclitaxel, a chemotherapy medication currently used to treat several cancers, e.g. breast and lung cancers, is selected as the model drug. The particles are comprised of a poly(lactic acid) that contains the drug of interest as the core that is decorated with cucurbit[7]uril functionalities on the surface, which in turn form inclusion complexes with adamantane functionalised PEG (Fig. 33A). Upon approaching the tumour (an environment of high oxidative stress), the particles undergo de-

PEGylation and penetrate the cancerous cell (Fig. 33B). A high concentration of glutathione (containing a disulfide bond) inside the tumour breaks down the core of the particles, and the drug is thus released in a targeted fashion (Fig. 33C). One advantage of the reported system is its high adaptivity resulting from its supramolecular assembly. Furthermore, the presence of cucurbit[7]uril on the surface of the particles enables the introduction of any adamantane functionalised shell structures to tailor the particles responsiveness for different disease

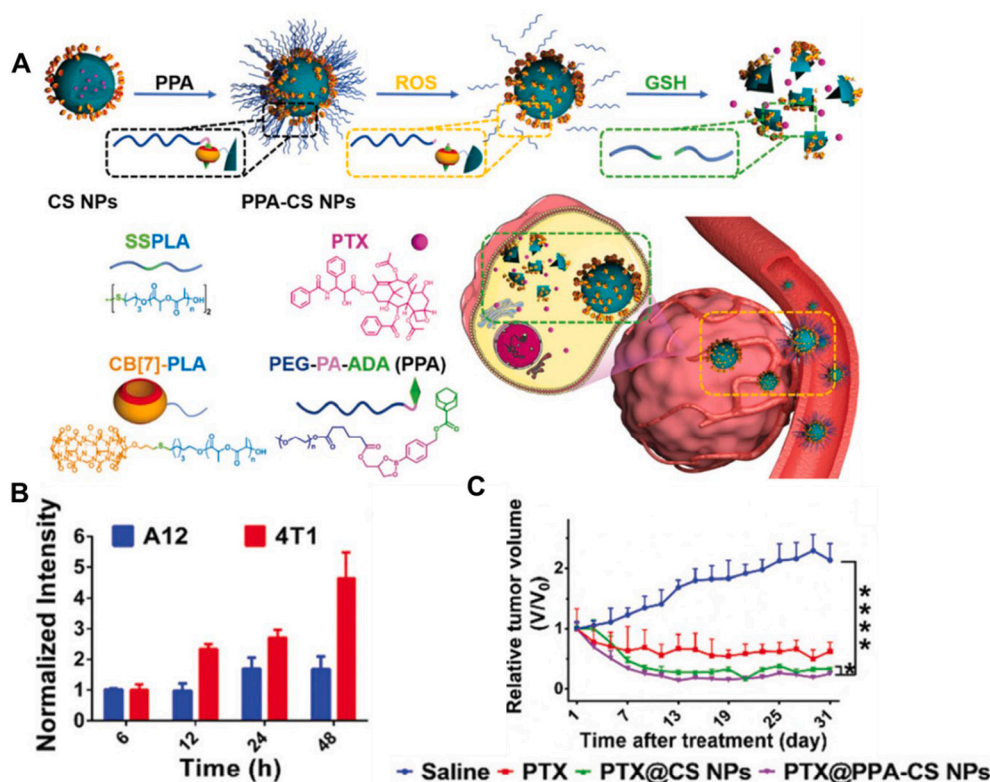


Fig. 33. A) A schematic image representing chemical structure and mode of operation of the anti-cancer supramolecular polymeric nanoparticles. B) Bar chart showing the penetration of the proposed supramolecular polymeric particles into healthy mouse-derived hepatocytes (A12) and mouse-derived breast cancer cells (4T1), proving that the high oxidative environment of cancerous cells increases the drug penetration by de-PEGylation. C) The results of exposing a 4T1-bearing mouse to different treatments, including saline (blue), direct commercially available Paclitaxel drug (red), Paclitaxel drug loaded in cucurbit[7]uril functionalised particles without PEG functionality (green) and Paclitaxel-contained particles with the pegylated surface. Reproduced from reference [216] with permission from the Royal Society of Chemistry.

states. A similar systematic approach is also proposed for protein delivery in which the intracellular glutathione and other amino acids are responsible for the release of the encapsulated protein [208]. The proposed approach that can be used for protein therapies involves a template-induced production of protein-polyphenol particles. The assembly of these microcapsules is generated by loading of the protein of interest and tannic acid in mesoporous silica nanoparticles (the template); upon removal of the template the protein is encapsulated within a polyphenol network. The surface charge of the particles is dictated based on the extracellular pH (for the transformation of the polyphenol hydroxy groups) and the isoelectric point of the protein. The negatively charged particles in extracellular medium (\sim pH = 7.4) can enter the acidic endosome. As a result of the change in the pH of the medium (from extracellular to endosomic), the surface charge of the particles was altered, and the particles can then escape from the endosome into the cytosol. It was found that unlike the micellar extracellular proteins, endogenous oxidized glutathione (GSSD), glutathione (GSH) and small peptide and amino acids can trigger the disassembly of the protein particles and induce the protein release inside the target cell. In these instances, the polymeric particles serve as both the drug carrier and a shield to protect the drug from unwanted and off-target release during blood circulation, reducing hepatotoxicity and improving drug efficacy. This is important for delivering small molecule drugs, such as bortezomib, since it is prone to rapid excretion before reaching the target site [217]. An additional approach to protect precious drug cargos is to take advantage of amphiphilic supramolecular assemblies and create a globular structure with the drug located at the core. A notable example is the block copolymer containing PEG and diethanolaminomethyl functionalised polystyrene synthesised by Nagasaki and co-workers

[218]. Upon forming the boric acid drug and diethanolamine conjugate, an amphiphilic polymer chain forms, which self-assemble into a globular structure with a hydrophobic (drug) core and a hydrophilic (PEG) shell. These supramolecular micelles are pH sensitive, and upon protonation the micelles break down and the drug is released. The proposed amphiphilic particle formation and encapsulation of the boronic acid drugs offer a facile procedure for delivering small molecule drugs, particularly in boron neutron capture therapy (BNCT), expanding the range of agents that can be utilised, e.g. phenylboronic acid and *p*-phenylene-diboronic acid.

Supramolecular polymers have been utilised to produce anti-kinking vascular grafts (Fig. 34) [219]. Vascular grafts are essential for patients suffering from kidney disease who rely on blood purification and do not have an adaptable vasculature. Currently available vascular grafts are prone to lumen failure under bending stress or sudden movement. In studies reported by Wu *et al.*, three-layered artificial vascular grafts were produced in which a layer of spiral reinforcement material was 3D printed and sandwiched between 2 layers of electrospun material [219]. Two different material systems were used to realise the design, a polycarbonate bisurea reinforced by strands of PCL and a supramolecular system of chain extended PCL-UPy reinforced by UPy-dicapped PCL (Fig. 34A). The advantage of the latter system was that the graft's mechanical properties were found to be improved without compromising its flexibility. Although the printed spiral reinforcing scaffold approach improved the mechanical properties and enhanced the polycarbonate bisurea system's anti-kinking characteristics, unfortunately, this formulation could prove problematic since the degradation of PCL is not compatible with the hydrogen bonding of the bisurea shells. In contrast, the supramolecular system layers comprise a hydrogen bonding

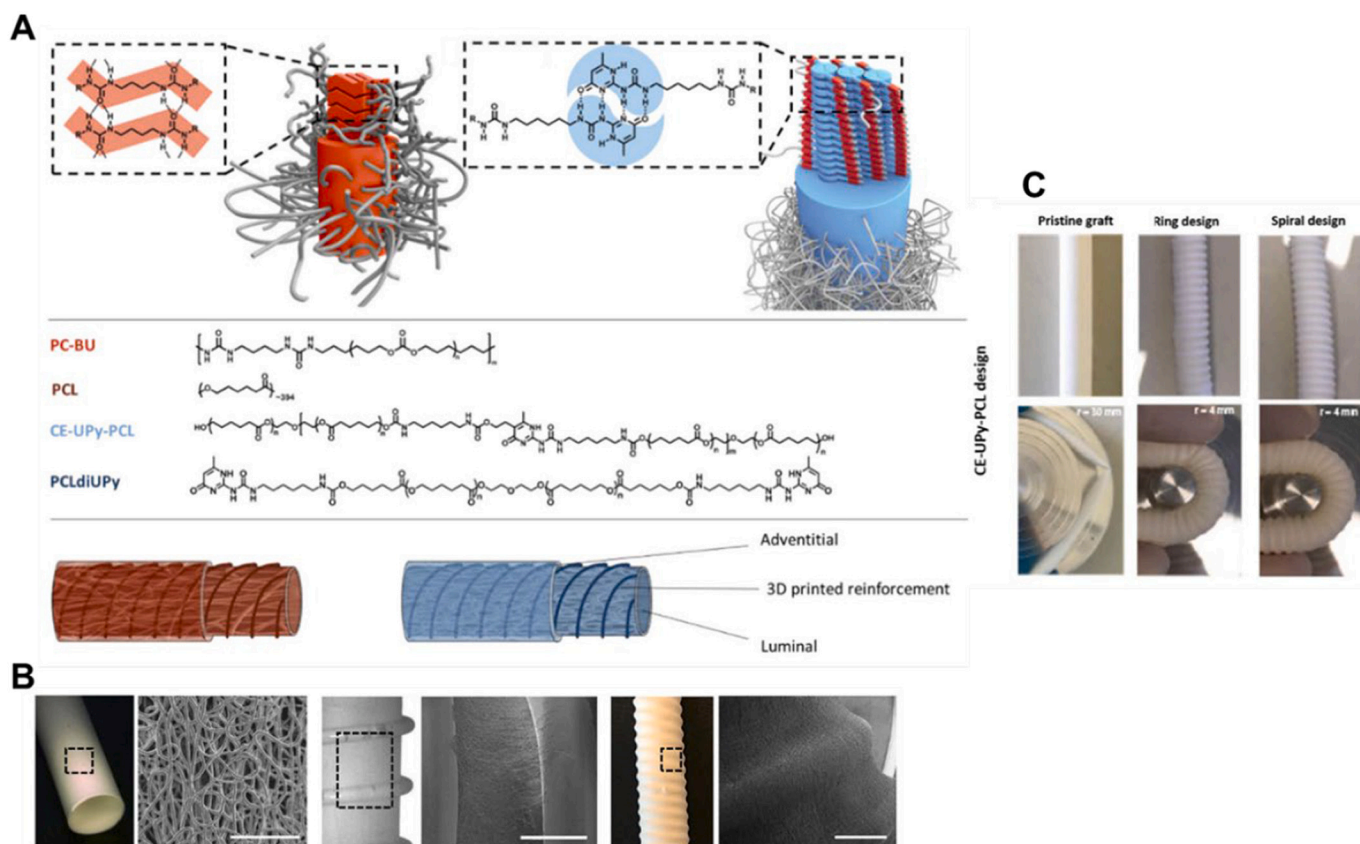


Fig. 34. A) Schematic representation of the 3-layered artificial graft design and the related non/- supramolecular materials. B) microscopic images of the supramolecular anti kinking graft, left to right; first electrospun layer (luminal), scale bar = 100 μ m, second 3D printed layer (reinforcement) and the third electrospun layer (adventitial). The scale bars represent 1 mm. C) Pictures of the supramolecular artificial vascular graft with 700 μ m thickness and the corresponding anti-kinking ability. The image shows a pristine electrospun graft without a 3D printed reinforcement layer (left), an electrospun graft featuring a reinforcing layer with ring geometry (middle), and the electrospun graft spiral reinforcing structure [219].

supramolecular network and degrade at a similar rate and via the same mechanism. Therefore, the supramolecular vascular graft is safer and more durable, making its implementation more appealing and feasible.

In 2021 the Stupp group reported a significant advance in the regenerative treatment of spinal injuries. In this study Álvarez *et al.* generated [220] a supramolecular peptide fibril scaffold system that featured two peptide sequences that promote nerve regeneration, one that reduces glial scarring and another that enhanced the formation of blood vessels. Using a mouse model to simulate a paralyzing human spinal cord injury, it was found that mutations in a tetrapeptide domain outside of the signalling regions were able to improve recovery of function by promoting intense supramolecular motion within the fibrils.

3. Conclusions and future perspectives

This perspective has used selected examples from the literature to show how supramolecular polymeric materials could positively impact on a range of commercial applications. This review has highlighted key examples that harness the rapid and reversible stimuli-responsive properties offered by the supramolecular bond: adhesives (Section 2.1), printable (Section 2.3) and healable materials (Section 2.4). However, as the field has matured, the supramolecular polymer architectures have become ever more complex, for example, rotaxanes within the main chain of the system to allow stress sensing (Section 2.7) or systems that permit targeted drug delivery (Section 2.9). Whilst these approaches offer functionality well beyond the scope of 'traditional' covalently bonded commodity polymers, their synthetic complexity does, however, come at a financial cost.

The challenge over the coming years is to balance the cost in terms of reagents and synthetic time with the improved functionality of the final, functional material to deliver products that the market can support. Running alongside this financial challenge, and in common with all synthetic chemistry is the expanding interest in 'green' chemistry. This is particularly important in polymer synthesis as the production scale is significantly greater than in the pharmaceutical industry. Presently, most supramolecular polymer chemistry is still seeking to demonstrate what is possible, with little consideration for the efficiency of synthesis or the origin of the starting materials (e.g. petrochemical feedstocks or renewable resources). This could be a real opportunity, because many of the potential applications demonstrated here are not seeking to replace a commercial material, but offer a new product. Therefore, building a 'green chemistry' [221] mentality into the design and scale-up of these polymers and products from the start could offer benefits in terms of a reduction in waste, solvent use and energy consumption, which may make the product more appealing to the customer, even if this comes at increased initial cost.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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