Chapter 1
Supramolecular Ionic Networks: Design and Synthesis

M. Ali Aboudzadeh

Abstract Supramolecular polymer networks are chains of low molecular mass monomers held together by reversible non-covalent interactions, such as hydrogen bonds, metal–ligand bonds, hydrophobic or $\pi-\pi$ stacking interactions. The reversibility and low energy bonding bring about additional features compared to conventional covalent polymers, which potentially lead to new properties such as improved processing, self-healing behavior, and stimuli-responsiveness. Whereas the use of (multiple) hydrogen bonds is leading the discoveries in this area, the emerging ionic chemistry has also been translated to the development of supramolecular assemblies based on ionic interactions. This approach provides exciting opportunities for synthesizing new supramolecular materials via manipulation of the type and strength of the ion pair as well as the number of interactions. In this chapter, the most relevant advances and current knowledge in design and synthesis of supramolecular ionic networks, including those prepared from low molecular weight molecules, polymers, or a combination of the two are briefly reviewed. Their flexible and simple construction is depicted via several examples and case studies. Finally, the important concerns and possible opportunities are explained to inspire critical discussions and boost further findings.

1.1 Introduction

Conventional polymers are long-chain molecules made up of repeating structural units linked through covalent bonds. They have been employed widely in ordinary life and advanced technologies for more than a half-century. In the last thirty years, the universality of reversible non-covalent interactions has been perceived with the evolution of supramolecular chemistry, defined by Lehn as the chemistry beyond molecules, who firstly reported the application of hydrogen bonds to create polymer

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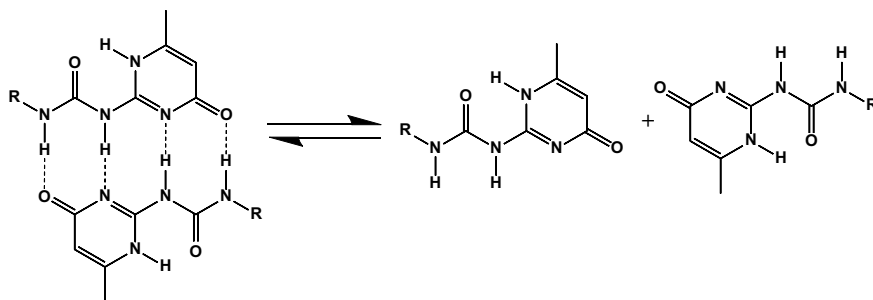e-mail: m.aboudzadeh-barihi@univ-pau.fr

Fig. 1.1 Network structure of the monomer (UPy) units connected by reversible hydrogen bonds. The UPy units form four hydrogen bonds to each other (dotted lines)

structures [1]. One important aspect of supramolecular chemistry is the application of clear-cut molecules or macromolecules and intermolecular forces to generate larger, more intricate chemical species with novel and extraordinary properties [2–4]. This discovery encouraged scientists to build up reversible alternatives for covalent polymers.

Nevertheless, in the beginning, it was not simple how to incorporate highly directional, amply strong, but still reversible interactions to direct small molecules to be assembled into polymeric patterns. Particular breakthrough was not reported until the pioneering work by Meijer et al. [5]. They assembled 2-ureido-4[1H]-pyrimidinone (UPy) units into extended chains by means of quadruple cooperative hydrogen bonds in an array and developed products with similar mechanical properties that until then could only be achieved with covalent polymers (Fig. 1.1). In such systems, by increasing the temperature the viscosity of the supramolecular polymers could decrease, indicating an exceptional thermo-responsiveness coming from reversible hydrogen bond interactions. This property allowed supramolecular polymeric materials to be easily processed.

Following this achievement and in recent years, many scientists have been studying and exploring the ability to utilize non-covalent intermolecular forces to build controlled supramolecular structures and tailor their properties. Among various supramolecular assemblies known, polymer networks are specifically interesting as their properties can be completely different from the properties of their covalently bonded counterparts or the individual macromers [6–8]. In particular, reversible binding through cooperative hydrogen bonds [9–11], ionic interactions [12, 13] and metal–ligand complexes [14, 15], etc. can lead to aggregation, gelation, or sudden viscosity changes that are triggered by changes in molecular concentration, pH, or temperature. Networks established through this approach have particular advantages over conventional polymer networks based on covalent bonding because they merge the features of traditional polymers with the reversibility of bonds that hold monomer segments. Nevertheless, when these reversible holding interactions are removed, for instance by heating, their elastic or rigid nature can be converted into
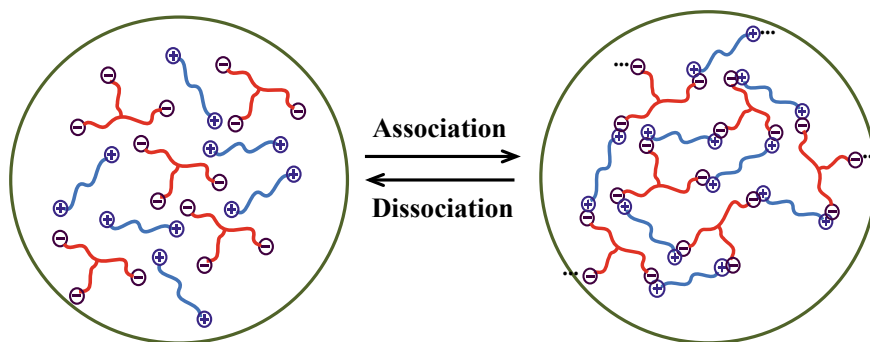
Scheme 1.1 Schematic of supramolecular polymer networks generated from non-covalent ionic interactions. The major difference from traditional polymer is the equilibrium between association and dissociation of the interactions

low viscosity small molecules [16]. These unique characteristics facilitate a new category of stimuli-responsive and functional polymers named supramolecular polymer networks [17].

Scheme 1.1 graphically shows a supramolecular polymer network made up of end-to-end chaining of low molecular mass oligomers. Similar to conventional polymers, supramolecular networks present analogous macromolecular properties in solutions as well as in bulk. However, because the connecting forces for their structures are reversible interactions, supramolecular networks still behave like small molecules when their reversible interactions dissociate with changing conditions such as heating or solvent switching.

One undesirable disadvantage of conventional polymers is their high melt viscosities as a result of their chain entanglements, which make them difficult to process. In contrast, supramolecular polymer networks generally exhibit a strongly temperature-dependent melt viscosity, which improves their processability in a less viscous state at temperatures only moderately higher than their melting or glass transition temperatures. The reversible properties of supramolecular polymers make them capable of self-repair or healing after disruption of the interaction, which opened a quite new research field in the last two decades. To obtain these novel features, the most challenging task is to design appropriate building block functionalities with synthetic accessibility and high stability. It is the aim of this chapter to present an overall view of the synthetic methods to create these new networks. Particularly, we start by presenting different types of supramolecular assemblies, and then we address the advances in the field of supramolecular ionic assemblies, including those composed of complementarily charged polymers, low molecular weight molecules, or a combination of the two. Finally, the motivation for further discoveries in this field and future perspectives are discussed.

1.2 Different Types of Supramolecular Assemblies

Supramolecular assemblies can be categorized on the basis of three different principles: (1) the physical nature of the non-covalent force that lies at the origin of the reversible interaction, (2) the type of structural monomer(s) used, for example, supramolecular polymerization of an A_2 monomer or an A-B type monomer, and (3) the Gibbs free thermodynamics which describes different mechanisms of supramolecular polymerizations and shows how the conversion is based on temperature, concentration, etc. Each classification has its own scientific merits [18]. In this chapter, we classify different supramolecular assemblies on the basis of the physical nature of the various types of interactions that can behave as driving forces for the design of large supramolecular assemblies. Important non-covalent interactions include hydrogen bonding, electrostatic interactions, metal–ligand complex, and π–π stacking. Some examples of supramolecular assemblies via different non-covalent interactions will be discussed. The electrostatic interactions as the main synthetic strategy in this chapter will be discussed in much more detail in the next section. There are still other non-covalent interactions that could lead to supramolecular structures, such as hydrophobic forces [19, 20]. Furthermore, some supramolecular networks may include more than one type of non-covalent interaction. Table 1.1 summarizes different noncovalent interactions involved in the formation of supramolecular polymeric networks [21, 22].

1.2.1 Hydrogen Bond-Assisted Supramolecular Assemblies

Hydrogen bonding is the most investigated interaction among all types of reversible bonds. Due to their excellent directional selectivity, hydrogen bonds are ideal for molecular engineering of desired polymer networks. The strength of hydrogen

Table 1.1 Bond strengths of the different non-covalent interactions used in construction of supramolecular assemblies in comparison to the one of covalent bonds

Reversibility	Bond Strength		Type of interaction
Irreversible	Strong	> 60 kcal/mol	Covalent bond
Reversible	Medium	20–60 kcal/mol	Reversible covalent bond (e.g., –S–S–)
			metal–ligand coordination
			ionic interaction
			multiple hydrogen bonds
	Weak	0–20 kcal/mol	Hydrogen bond
			π–π stacking
			Hydrophobic interaction

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bonding depends on temperature, pressure, solvent, bond angle, and environment. It is worth remarking that the strength of a hydrogen-bonding motif is governed by the number of individuals involved hydrogen bonds. A higher number of hydrogen bonds generally signify stronger hydrogen bonding. Supramolecular assemblies based on hydrogen bonding gave rise to an array of novel materials. Following some examples are reviewed.

Meijer et al. reported thermal reversible polymers through developing ureidopyrimidinone (UPy) group with a bonding constant K of $6 \times 10^7 \, M^{-1}$. They observed that the building blocks are held together by UPy hydrogen bonds at room temperature resulting in a flexible polymer. While by increasing the temperature, UPy hydrogen bonds break, the building blocks lose their connections and the material behaves like a viscous liquid. This dramatic phase and property transitions induced by the dynamic nature of hydrogen bonds bring about a unique behavior for UPy groups [23].

Long et al. were capable of pairing UPy side-groups into linear poly(butyl acrylate)s to achieve a novel thermoplastic elastomer material. Mechanical studies revealed that melts of UPy consisted of linear poly(butyl acrylate) chains that act as a rubbery elastomer at room temperature, bearing a classical elastomer Young's modulus at about hundreds of kPa. Whereas at elevated high temperatures (80 °C), the Young's modulus decreased considerably, behaving like a viscous polymer melt. The authors attributed this novel effect to the dynamic nature of UPy hydrogen bonds and they concluded that at low temperature, UPy groups are attached together by means of hydrogen bonding serving as crosslinking junctions for the polymer network. At high temperatures, UPy hydrogen bonds dissociate, the linear poly(butyl acrylate) chains lose their connectivity and consequently flow again like a melt [24].

In another interesting example, a self-healing supramolecular elastomer based on multiple hydrogen-bonding interactions was developed by Leibler et al. They initiated their approach with vegetable-based fatty diacids and triacids, then the acid groups were condensed with a controlled excess of diethylenetriamine. In the end, the obtained product was reacted with urea leading to various oligomers with multiple self-complementary hydrogen bonding sites. The new resulting plastic-like material showed a glass transition temperature (T_g) at about 28 °C. Above this temperature, the material displayed typical characteristics of elastomers, i.e., it was deformed by applying stress and recovered its shape when the force is removed. At even higher temperatures (> 160 °C), the material could flow like a viscous liquid. In contrast to classical rubbers, it exhibited excellent self-healing abilities as depicted in Fig. 1.2. Once the cut parts were put in contact together, the material was capable of self-healing with time through rebinding the fractured hydrogen bonds [25–27].

Similar to this study, Odriozola et al. reported a covalently cured poly(urea–urethane) elastomeric network with self-healing ability at room temperature which was achieved through combination of dynamic covalent bonds with hydrogen bonds with superior mechanical strength [29]. The significant self-healing ability of this system could be associated with two structural features: metathesis reaction of aromatic disulfide which is in constant exchange at room temperature [30, 31] and two existing urea groups, capable of forming a quadruple hydrogen bond (Fig. 1.3).
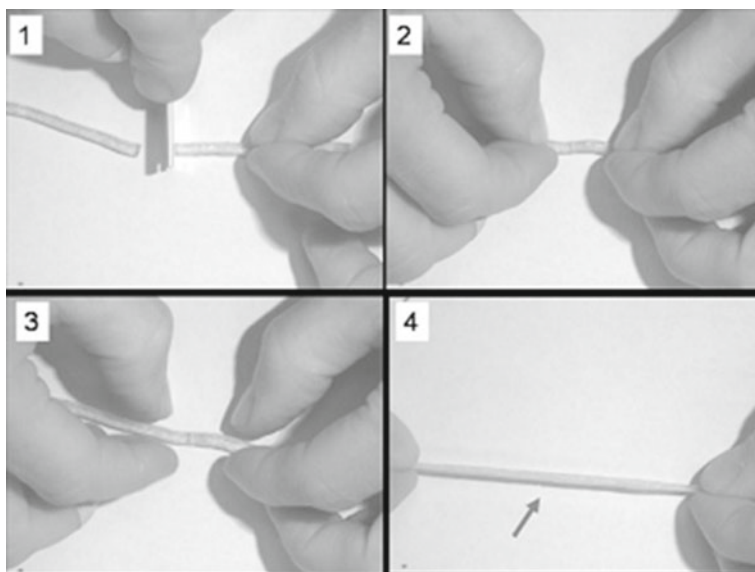
Fig. 1.2 Self-healing supramolecular elastomer developed by Leibler et al. Reproduced with permission from the Ref. [28] Copyright (2015) (Wiley)
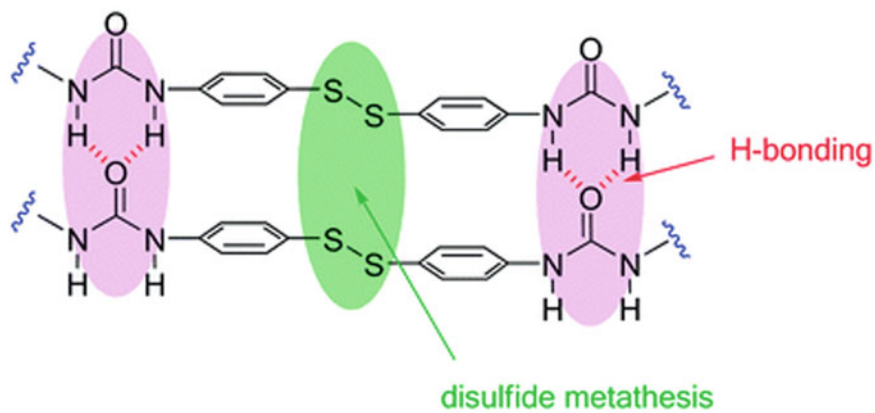

Fig. 1.3 Proposed bonds involved in the self-healing material developed by Odriozola et al. Reproduced with permission from the Ref. [28] Copyright (2014) (Royal Society of Chemistry)
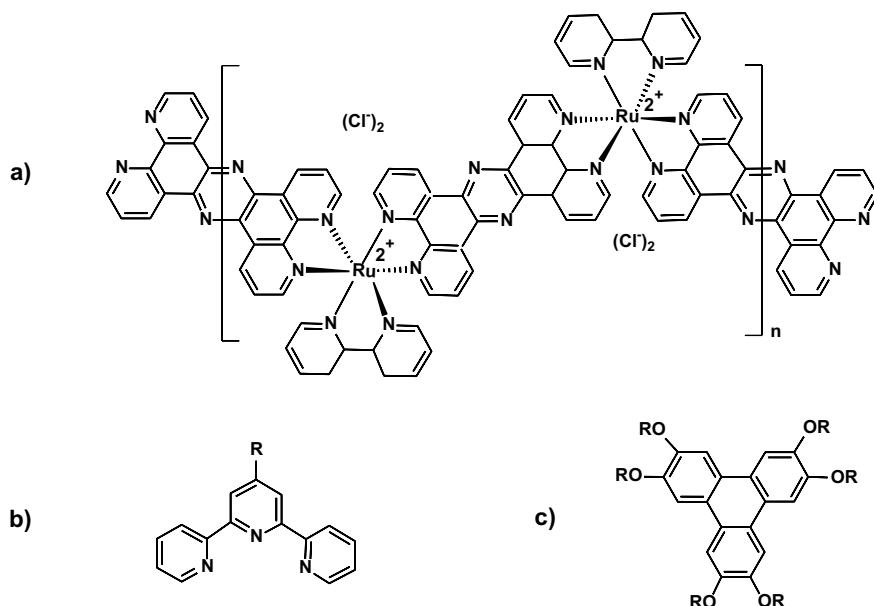
Fig. 1.4 **a** An example of Ruthenium(II) coordination polymer complex, **b** a model structure of terpyridine ligand and **c** molecular structure of triphenylene

1.2.2 Metal–Ligand Induced Supramolecular Assemblies

Reversible metal–ligand complexes are extensively employed in molecular self-assembly and host–guest recognition applications [32–34]. Ruthenium (II) coordination polymers are one of the first examples of metal–ligand induced supramolecular assemblies [35, 36]. The Ruthenium (II) pyridine type ligand complex is well known and relatively stable. By designing the appropriate monomer structure, Ruthenium (II) coordination polymers can be assembled (Fig. 1.4a). Terpyridine is another important class of ligands used in metal–ligand-induced supramolecular assemblies [37–40]. A model structure of this ligand is presented in Fig. 1.4b. Similar to the structure shown in Fig. 1.4a, terpyridine is able to bind various metals such as Fe^{2+}, Zn^{2+}, Ru^{2+}, Co^{2+}, etc. to form bisterpy metal complexes [16].

1.2.3 Supramolecular Assemblies Based on π–π Stacking Interaction

Many conjugated or aromatic molecular structures can undergo π–π stacking secondary interactions. This type of interaction mostly induces discotic stacking which results in crystalline or liquid crystalline state. Supramolecular assemblies

can be constructed by means of π–π stacking. In this regard, triphenylenes are the most investigated disc-shaped molecules to form supramolecular structures [16]. The general structure of triphenylene is presented in Fig. 1.4c, in which changing the pendant R groups into appropriate side chains allows triphenylenes to generate aggregated polymeric columns in either water phase or organic solutions [41–44]. Burattini et al. developed an original healable polymer network formed by π–π stacking interactions between pyrenyl end-groups and chain folded polyimides [45–47].

Moreover, π–π stacking interaction is very prevalent in copolymers or conjugated polymers. The cooperative π–π interactions inside some polymers lead to generation of new supramolecular complexes which could have promising applications in the fields such as transistor electronics, light-emitting cells, and photovoltaic devices [48–50].

1.3 Supramolecular Assemblies Based on Electrostatic Interactions

Non-covalent electrostatic interactions via ion pairing play a major role in the design of supramolecular assemblies, especially in an aqueous environment wherein due to the water-solubility of the charged groups, they could form strong electrostatic interactions. Rise of ionomers and polyelectrolytes in the early twentieth century led to the concept development and application of electrostatic interactions in polymer structures. Ionomers are copolymers in which an ionic group (*e.g.,* carboxylate) is loaded into a polymer at a small quantity (generally < 15%) as a means for altering polymer properties. These components were commercially available in the 1950s. Mixtures of ionomers with randomly distributed positively and negatively charged groups can lead to formation of materials held together by electrostatic interactions. For example, van der Zwaag and Varley have reported different classes of ionomers and their self-healing behavior [51–53].

Polyelectrolytes are similar to ionomers but they have higher number of ionic groups (high charge density) and most of them are soluble in aqueous solution [54]. Polyelectrolytes are divided into three types: polyanions, polycations, and polyampholytes. Polyanions and polycations have negatively and positively charged groups, respectively and they possess extended chain conformations due to repulsive interactions between like-charged groups. Polyampholytes are ionic polymers having both positive and negatively charged groups and they have compact conformations because of attractive interactions between the unlike charges. The high quantity of charged groups on the backbones of polyelectrolytes (polycations or polyanions) attracts many counterions to its nearby neighborhood (counterion condensation) [55–57].

Ionomers and polyelectrolytes, with their ionic recognition groups, are extensively used to generate supramolecular assemblies. In spite of their long history, interesting functionality, and diverse structures available to use, electrostatic interactions have not been as widely studied as metal–ligand coordination and hydrogen bonding

in the field of supramolecular materials. Compared to other non-covalent analogs, ionic interactions have particular characteristics as follows. First, they are stronger and less directional [21]; second, they may develop larger agglomerated structures dependent on the steric surroundings of the ion pair [58, 59]; third, coulombic interactions are asymmetric and sensitive to the local constant of the environment they are in [60]; and fourth, ionic interactions are simply adjustable via the combination of different cationic (e.g., primary or secondary amine, quaternary ammonium) and anionic structures (e.g., sulfonate vs. carboxylate) that are available through straightforward chemistry. In particular, advantages of working with electrostatic bonds alone or in combination with other non-covalent interactions are that a considerable number of molecules and macromolecules are ready for use and that the preparation methods are simple and appear generalizable [22].

In the following subsections, advances in supramolecular ionic networks from synthetic aspects are reviewed. These networks are classified if they were prepared from low molecular weight molecules, polymers, or a combination of the two. This type of classification was first introduced in a review paper published on this topic in 2013 [22]. Then in the next chapter, we will review the dramatic impact of molecular design on how these ionic interactions could control the bulk properties.

1.3.1 Supramolecular Ionic Assemblies from Low Molecular Weight Molecules

Low molecular weight molecules can attach to each other through non-covalent interactions to form linear or polymer network systems. The challenges related to applying ionic interactions between low molecular weight molecules for the balanced engineering of supramolecular assemblies include first, the relative deficiency of specificity between counterparts [21] and second, the isotropy of Coulombic potentials between discrete charges, which compromises even the validity of considering stoichiometric 1:1 pairwise interactions between oppositely charged partners [61].

Contrary to supramolecular assemblies formed by polymers, low molecular weights molecules can induce faster equilibration and the obtained assemblies may exhibit a higher degree of mesoscopic order [22]. In one of early studies, Hosseini et al. synthesized a self-assembled structure by combining ion-pairing electrostatic interaction and hydrogen bonding. In this study, a phthalate dianion was reacted with a dicationic compound composed of two cyclic amidinium groups with four hydrogen bonding donor sites to form a linear polymer chain (Fig. 1.5a). X-ray study confirmed the proposed linear structure if the anion was terephthalate or isophthalate [62]. The same research group showed that by adding two carboxylic acids to the anion (using pyromellitate dianion), a self-assembled crystalline 2D molecular network can be achieved (Fig. 1.5b) in addition to the linear polymer chains [63].
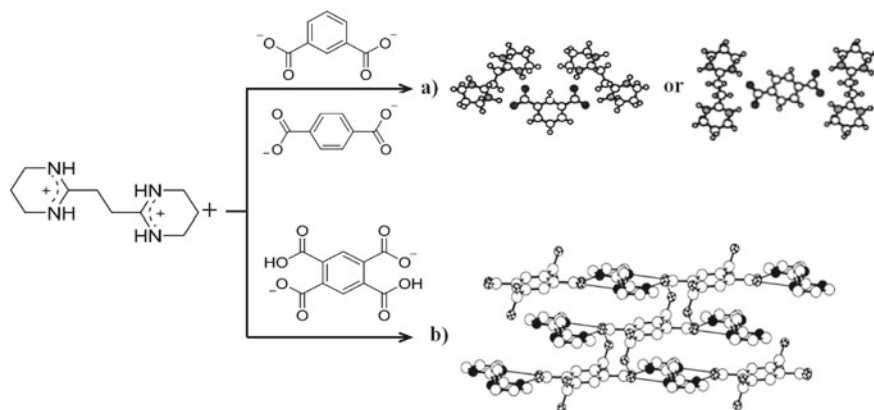
Fig. 1.5 Chemical structures of dicationic cyclic amidinium, phthalate dianions, pyromellitate dianion and X-ray structures of the resulting **a** linear or **b** 2-D network assemblies. Adapted with permissions from the references [61, 62] Copyright (1994, 2001) (Royal Society of Chemistry, Elsevier), respectively

In 2008, Grinstaff et al. suggested a distinct, practical, and complementary strategy for the construction of ionic networks from entirely non-coordinating ionic pairs, particularly those discovered from ionic liquids chemistry. These scientists combined a tetraanion, ethylenediaminetetraacetate (EDTA^{4-}), and a dication, consisting of two covalently linked tetraalkyl phosphonium components to assemble an ionic liquid. Since there were adequate units of cationic and anionic groups on each species and assuming that the Coulombic forces are governed by two-by-two inter-actions among individual cationic and anionic groups, the expected complex to be formed was effectively a supramolecular ionic network (Fig. 1.6). To check the generalizability of the approach, the authors replaced EDTA with *para*-tetracarboxy-5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H$_2$TPP^{4-}) aiming at developing an ionic porphyrin assembly. As result, they observed that porphyrin sustained its fluorescence suggesting that ionic networks having particular functional building blocks maintain their original features [64]. Combining the reversibility of the disulfide bond and the use of ionic interactions, this research group designed a crosslinked ionic network based on disulfide diphosphonium ionic liquid and tetraanion (EDTA^{4-}). By applying external stimuli such as temperature or inducing a mild redox reaction, the resulting ionic network underwent a reversible transition from a network to a non-network state [65].

Whereas this pioneering study made use of intricate ionic liquid units like alkyl phosphonium dications, Aboudzadeh et al. presented a simple strategy to synthesize supramolecular ionic networks through employing commercially accessible di- or trifunctional amines and carboxylic acids (Fig. 1.7a). The basic chemical reaction that they used was proton transfer, a reaction mechanism step applied in constructing protic ionic liquids, also recognized as acid–base complexation. Protic ionic liquids are readily synthesized through the neutralization and subsequent proton transfer
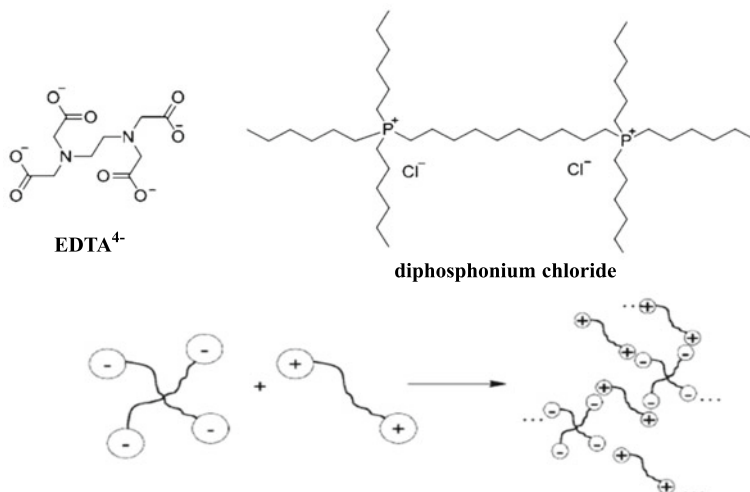
Fig. 1.6 Formation of a supramolecular ionic network reported by Grinstaff et al. (up): chemical structures involved; (down): schematic diagram of network formation. Reproduced with permission from Ref. [22] Copyright (2013) (Wiley)
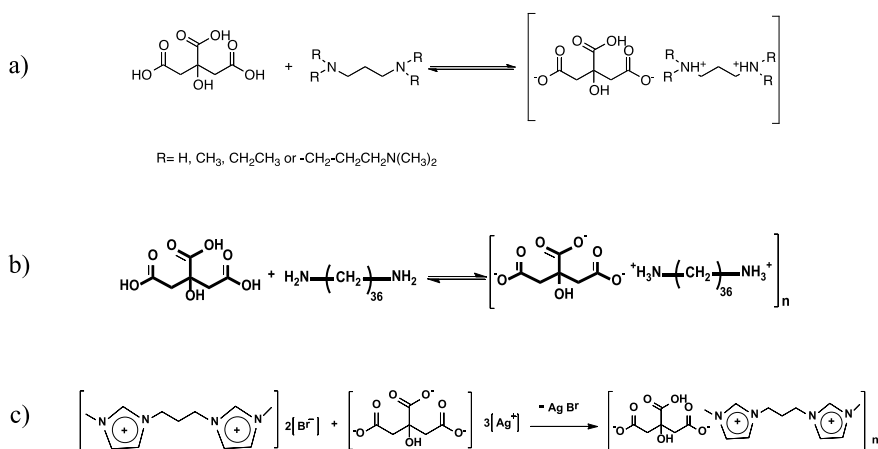

Fig. 1.7 Proposed reaction pathway for the synthesis of supramolecular ionic networks based on citric acid and **a** commercially available di- or trifunctional amines **b** a fully renewable C36 biobased diamine (Priamine 1074) and **c** geminal dicationic ionic liquids. Reproduced with permissions from the references [70–72] Copyright (2012, 2014, 2013) (American Chemical Society, Wiley, Royal Society of Chemistry), respectively

between a base and a Brønsted acid [66–68]. A group of (di-/tri-) functional primary-
and tertiary amine bases and (di-/tri-) functional carboxylic acids were tested by
these authors. In all selected combinations, the reactants were added all at once
in an equimolar quantity and stirred together at room temperature in the presence
of a solvent, such as water or methanol, to eliminate the issues of the exothermic
neutralization reactions. The reactions were quick and after solvent removal, a
series of products were synthesized effortlessly. Characterizing the products using
nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectro-
scopies, the authors obtained a direct evidence of proton transfer reaction between
the carboxylic acid and the amine. The important advantage of this synthetic method
was that it did not require a previous ionic-monomer synthetic stage [69]. Citric
acid, among all examined carboxylic acid molecules, displayed a promising ability
leading to the formation of supramolecular ionic networks with remarkable ionic
conductivity and self-healing characteristics. The probability of involving hydrogen
bonding in these systems was studied by the authors as well. They performed a
control test in which instead of citric acid, the equivalent triol (glycerol) was reacted
with a diamine molecule (1,3-propanediamine in this case) at mole ratio 1:1. As the
product of this reaction, a liquid with very low viscosity was achieved, suggesting
the small impact of the hydrogen bonding in comparison to the ionic interactions
[70].

Moreover, the same authors via the same synthetic strategy developed supramolec-
ular ionic networks fully based on chemicals coming from renewable feedstock
(Fig. 1.7b). In this study, Priamine 1074 a biobased fatty diamine molecule (as the
dication source) was reacted separately with a series of naturally occurring carboxylic
acids such as malonic acid, citric acid, tartaric acid, and 2,5-furandicarboxylic acid
[71]. These efforts allowed incorporation of natural products such as citric acid
in the design of supramolecular networks. Following these reports, these scientists
also achieved another type of supramolecular ionic network based on citrate anions
and the most important types of dicationic ionic liquids such as di-imidazolium,
di-pyridinium, or di-pyrrolidonium (Fig. 1.7c) [72]. The properties (rheological,
conductivity, self-healing, etc.) of these three categories (shown in Fig. 1.7) will
be fully discussed in chapter two. However, these ionic networks possessed certain
intrinsic issues related to the constituent carboxylate compounds such as water sensi-
tivity, poor thermal stability temperature, and low ionic conductivity. Therefore, in
order to overcome these weak points, the same research group developed another
approach to synthesize supramolecular ionic networks. This approach involved first
the preparation of ionic monomers which contained highly delocalized attached
(trifluoromethane-sulfonyl)imide $-SO_2-N-SO_2-CF_3$, or (propylsulfonyl)methanide
$-SO_2-C(CN)_2$, or (cyano-propylsulfonyl)imide $-SO_2-N-CN$ anions (Fig. 1.8 left).
The route to synthesize these compounds was similar to the reported procedure in
the case of methacrylic anionic monomers [73]. In the second step, these dianions
were combined with geminal di-imidazolium dications as the building blocks for
preparation of the targeted supramolecular ionic networks. Although most of the
synthesized networks were semi-crystalline (Fig. 1.8 right, **a**, **b** and **d**), amorphous
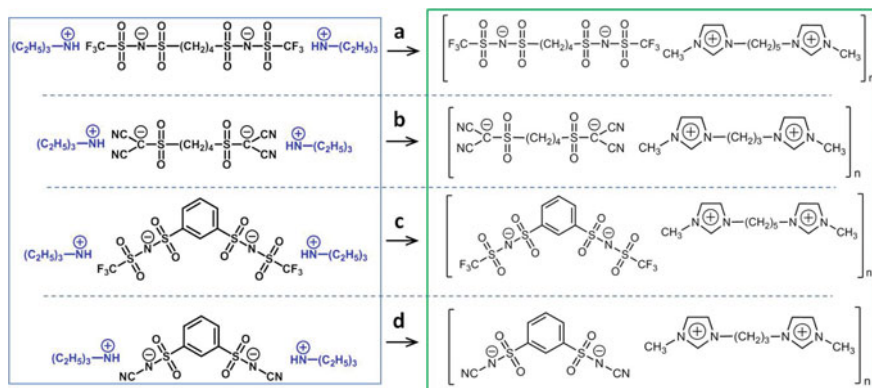
Fig. 1.8 Left) Ionic monomers containing highly delocalized attached $-SO_2-N-SO_2-CF_3$, $-SO_2-C(CN)_2$, and $-SO_2-N-CN$ anions. Right) Structures of supramolecular ionic networks based on highly delocalized dianions. Adapted with permission from the reference [74] Copyright (2015) (Royal Society of Chemistry)

networks were also obtained using aromatic asymmetric dianions (Fig. 1.8 right, **c**) [74].

In another study, supramolecular porous ionic networks were designed and prepared through one-pot procedure, involving the quaternization of triimidazole triazine with cyanuric chloride followed by hydrolysis and in-situ assembly (Fig. 1.9). The authors declared that the process of ionic crosslinking formation forces their chain conformation to be fixed to some extent, and this conformation fixation by ionic crosslinking is one of the reasons to create porosity [75].
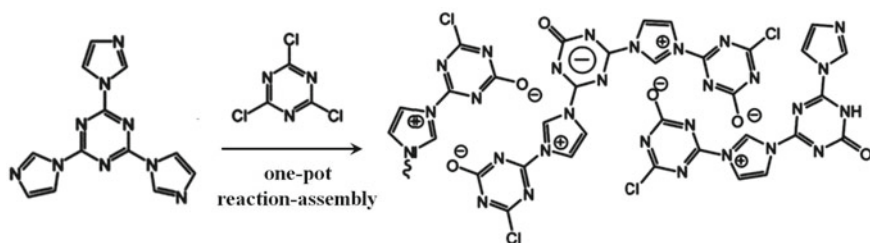

Fig. 1.9 Reaction pathway for the synthesis of supramolecular porous ionic network developed by Huang et al. Adopted with permission from the reference [75] Copyright (2016) (Royal Society of Chemistry)

1.3.2 Supramolecular Ionic Assemblies from Low Molecular Weight Molecules and Polymers

Appropriate selection of a low molecular weight molecule (*e.g.*, lipids, peptides, dyes, or surfactants) to be paired with a polymer via electrostatic interactions can provide an approach to developing specific structures with excellent functions. Polyelectrolyte–surfactant complexes are one of the early investigated assemblies in this category. These complexes combine the properties of polymers (mechanical strength and viscoelasticity) and surfactants (formation of highly hierarchical mesophases) [76, 77]. In these complexes, the ionic interaction between the ion pairs, as well as the hydrophobic interaction between the hydrocarbon tails of the surfactant, bring about thermodynamically stable ordered phases or aggregates depending on the preparation method [78].

In one of pioneering studies, Antonietti et al. synthesized and characterized a self-assembled complex formed between poly(styrenesulfonate) and alkyltrimethylammonium cations with different alkyl tails by common precipitation in water. Similarly, copolymers of poly(alkylacrylamide) and poly(acrylic acid) were assembled with surfactants to form ordered structures. Considering the simplicity of the "synthesis" and the availability of the starting materials, the authors predicted promising applications for this new class of products [79, 80]. The complexation of natural lipids such as diverse soybean-lecithins with a cationic polyelectrolyte, poly(dimethyldiallylammonium chloride) (PDADMAC), was carried out by the same research group too. The authors considered such systems as "Plastic Membranes" to mimic the structure of the cell membrane [81–83]. In another study, Thünemann et al. investigated the mixture of PDADMAC and surfactants with a pendant trimethylsilyl moiety complex and found smectic A-like lamellar mesophases and low energy surfaces (20 and 36 mN/m) for them. Due to the low surface energy and the high mechanical deformability of the complexes, the authors introduced them as flexible water-repellent coatings [84]. This scientist in another structural study using X-ray scattering showed that poly(ethylenimine) and n-alkyl carboxylic acids produce lamellar structures which are dependent on composition of the coordinating acid as well as the ratio of the two components [85].

Cationic dendrimers and oppositely charged small divalent organic ions in solution can give rise to stable functional supramolecular architectures. For example, Gröhn et al. introduced a simple route to prepare nanoparticles with cylindrical or spherical shapes through electrostatic self-assembly between poly(amidoamine) (PAMAM) dendrimer ions and the divalent 1,4- or 2,3-naphthalene dicarboxylic acid in methanolic solution (Fig. 1.10) [86, 87]. Use of dendritic macromolecules to create macroscopic ionic networks was reported in another study by Hvilsted et al. too. In this study, the networks were prepared by simple mixing of stoichiometric amounts of carboxylic acid-telechelic poly(ethylene glycol)s (DiCOOH-PEG) at different molecular mass (M_n ~ 250, M_n ~ 600, and M_n ~ 4800) with poly(propylene imine) (PPI) dendrimers or simpler amines such as tris(2-aminoethyl)amine (TAEA) or hexamethylene diamine (HMDA). These structures are shown in Fig. 1.11.
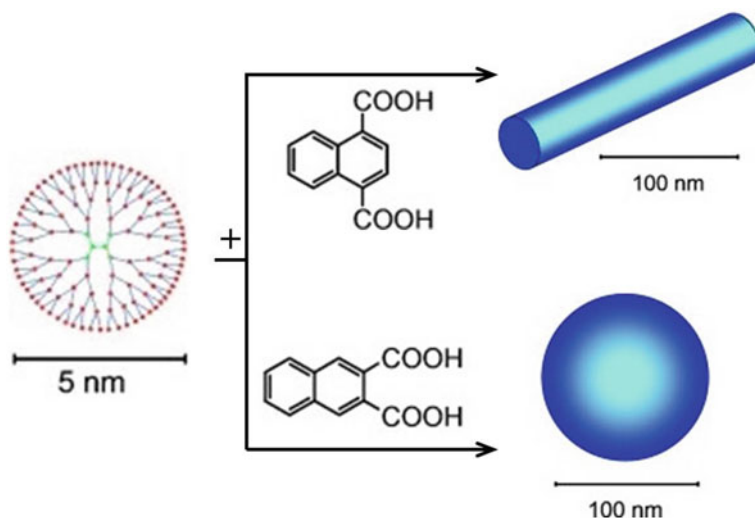
Fig. 1.10 Schematic representation of a PAMAM dendrimer, formulas of the counterions, and different shapes of the resulting nanoparticles. Adopted with permission from the Ref. [86] Copyright (2008) (Wiley)
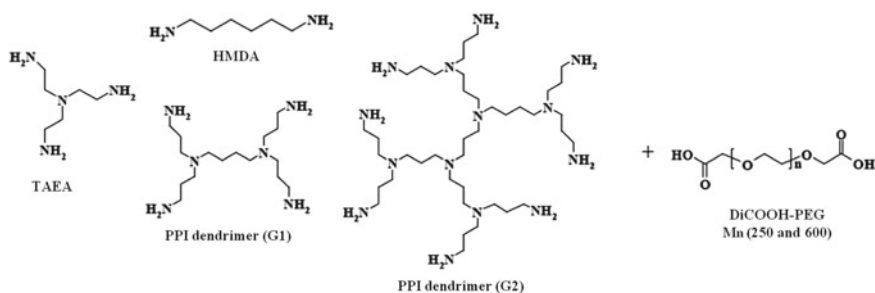
Fig. 1.11 Structures of PPI dendrimers, amines, and carboxylic acid end-functionalized PEGs DiCOOH-PEG that have been used to create the supramolecular ionic networks by Hvilsted et al. Reproduced with permission from the Ref. [88] Open access under a CC BY 4.0 license, https://creativecommons.org/licenses/by/4.0/

Performing a comprehensive ^{1}H NMR analysis, it was revealed that only the four primary amines of the PPI dendrimer (with molecular formula $C_{16}N_6H_{40}$) residing at the periphery take part in the ionic network formation [88].

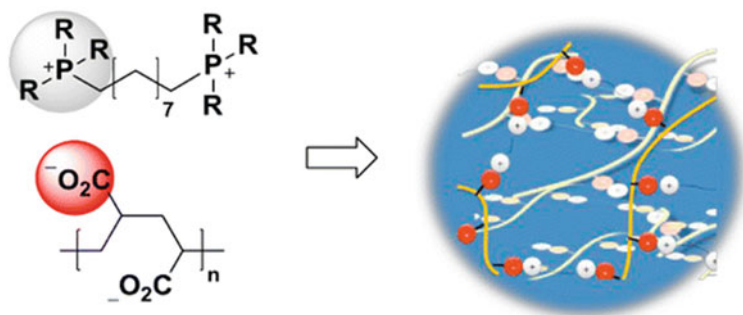**Fig. 1.12** Schematic representation of supramolecular polymer networks formed through ion pairing between phosphonium dications and the multianion, poly(acrylic acid). R = butyl, hexyl, or octyl. Reproduced with permission from the Ref. [90] Copyright (2012) (American Chemical Society)

Building upon these results, Grinstaff et al. investigated a self-organizing poly-electrolyte, a polymerized phosphonium ionic liquid, and mixed this polymer with different carboxylic acid-containing surfactants to form ordered structures. Depending on the number of ionic interactions as well as the nature of the anionic surfactant, the complexes exhibited completely different features including a brittle material, a rubbery ball that bounces, or a sticky fiber [89]. In most of the aforementioned studies, the charge stoichiometry is held at one to one (*i.e.*, each charge on the polymer is paired with a single charge species). Substituting the mono anion (or cation) with a multivalent anion (or cation) produces a polymeric network assembly. In this context, the same authors synthesized network structures by the complexation of various phosphonium dications with the multianion, poly(acrylic acid). In this study, the alkyl chains around the phosphonium dication were altered from butyl, hexyl, to octyl in order to explore the effect of sterics and ion pairing on the resulting macroscopic properties of the assemblies (Fig. 1.12). This study revealed insight into the structure–property relationship for the design of ionic supramolecular assemblies with desired properties [90].

Utilization of short peptides with a sequence-ordered chemical structure can bring about supramolecular networks a special functionality [91]. Among these short peptides, those containing fluorenylmethyloxycarbonyl (Fmoc) functional groups and bearing phenylalanine amino acids are prone to self-assemble via $\pi-\pi$ interactions between aromatic groups. In a recent study, Boulmedais et al. presented an approach to trigger and regulate the self-assembly of Fmoc-FFpY peptides (F: phenylalanine; Y: tyrosine; p: PO_4^{2-}), through direct electrostatic interactions with a polycation (polyallylamine hydrochloride), which yielded hydrogels without dephosphorylation of the peptides. The authors suggested that electrostatic interactions between the charged amine groups of the polycations and the phosphate groups of the peptides lead to the generation of core−shell cylindrical structures in which

flexible polycation chains decorate the micellar aggregates of Fmoc-FFpY peptides [92].

1.3.3 Supramolecular Ionic Assemblies from Polymers

Oppositely charged polymers can be used to develop different classes of self-assembled architectures governed by ionic interactions. The resulting supramolecular structures are commonly regarded as polyion assemblies. Their self-assembly capabilities bring about ordered mesoscopic scaffolds such as membranes, capsules, flocculants, and micelles by simple blending processes. A pioneering work on construction of supramolecular ionic assemblies from polymeric building blocks was carried out by mixing poly(vinyl-N-butylpyridinium bromide) and sodium poly(styrenesulfonate) together and studying the properties of the resultant polyanion-polycation complex [93]. Another early example reported by Miekka et al., in which sodium poly(styrenesulfonate) was also reacted with poly(vinylbenzyltrimethylammonium chloride) in dilute aqueous solution. As the product of the reaction, a water-insoluble extremely thin film was formed at the two-solution interface which contained equivalent quantities of each polyelectrolyte. The film displayed high diffusivity against salts such as sodium chloride, indicating a potential application as semipermeable membranes or as a solid electrolytes [94]. Depending on the concentration of the polyion solutions, the molecular weight of the polymers, pH, and the ionic strength, such complexes could be soluble in water or they could precipitate due to charge neutralization. Based on this fact, Kataoka and Harada developed polymeric micelles through spontaneous formation between a PEG-polycation block copolymer and a PEG-polyanion block copolymer in an aqueous solution. The authors chose biodegradable poly(Llysine) and poly(aspartic acid) as the polycation and polyanion blocks in the copolymer, respectively with the intention of making these polymer micelles as a promising vehicle for the delivery of various charged compounds to the body [95].

Different charged compounds can be used for the formation of supramolecular assemblies such as DNA, small interfering RNA, charged proteins, dendrimers, etc. [96–99]. In this context, these assemblies could be excellent candidates for the transport and delivery of biological agents since molecules such as DNA and proteins can be easily incorporated via ionic interactions. One of the earliest studies was the complexation between polyethyleneimine (PEI) and DNA reported by Boussif et al. The authors stated that every third atom of PEI is a protonable amino nitrogen atom, which makes the polymeric network an effective "proton sponge" at virtually any pH. This fact plus its low cytotoxicity makes PEI a promising vector for in vitro and in vivo gene therapy and delivery [100].

Viral gene vectors are considered the leading vehicles for delivering new genetic code to cells with outstanding results in multiple clinical tests [101]. To address the safety and manufacturing issues of viral vectors, a wide range of cationic polymers (associated with DNA via electrostatic interactions), have been studied as alternatives

due to their relatively low cost and tunability [102–107]. In this regard, the reader is referred to some comprehensive reviews on this topic [108–110].

Ionic dendrimers are the classical examples of rigid-rod and globular-shaped polyelectrolytes. Unlike linear polyelectrolytes, their ionic side chains decrease the degrees of freedom. Charge neutralization during the formation of supramolecular assembly shrinks the hydrodynamic volume, but the original globular or rod shape of each polymer is maintained. Aida et al. presented the first study on electrostatic self-assembly between negatively and positively charged dendrimers that contain within their frameworks a fluorescence probe. They observed that only globular-shaped particles or precipitates are formed by mixing two oppositely charged dendrimers [111]. Aida et al. also reported another interesting study, in which environmentally friendly 3D network hydrogels based on electrostatic interaction were formed. These gels were prepared using a PEG chain with cationic G3-dendrons on each end (G3-binder, 3 = generation number), mixed with negatively charged clay nanosheets (CNSs) that were dispersed by sodium polyacrylate (ASAP). G3-binder had two dendron units, which were decorated with multiple guanidinium ion pendants on their peripheries (Fig. 1.13). Multiple dendrons bind to each clay nanosheet, forming a free-standing gel that can self-heal and be remolded [112] (Fig. 1.13). In a follow-up study, the same research group prepared similar supramolecular hydrogels by using linear ABA triblock copolyethers carrying guanidinium (Gu⁺) groups at the side-chain termini of A blocks, while comprising a flexible PEG linker as the central B block. These hydrogels were as tough as the dendrimer-based gels, but the linear binders could be obtained by much less complicated syntheses from starting materials that were readily available [113].

Preparation of supramolecular ionic assemblies via acid–base complexation between functionalized polymers has been reported in some studies. For example, Matsushita et al. reported polymer blends made from carboxylic acid-terminated poly(dimethylsiloxane) (PDMS) and hyperbranched PEI. The parent polymers were both liquids and almost colorless at room temperature, while the blend samples had a yellow color originating from the redshift of the absorption band in a UV–vis region and looked more viscous due to acid–base complexation [114]. Furusho et al. reported a material developed by blending telechelic carboxylic acid-terminated polybutadiene and a linear polyamidine having N, N-di-substituted acetamidine group in the main chain. Charge interaction between the carboxylic acid and amidine groups led to the formation of a solid ionic network, which was not seen when the polyamidine was exchanged for PEI. Considering the high stability of amidinium-carboxylate salt bridge, the authors introduced it as an efficient and attractive non-covalent crosslinking concept [115]. In another study, Xu et al. designed a self-healing and thermoreversible rubber network by self-assembly of complementary polybutadiene oligomers bearing amine and carboxylic acid functionalities through reversible ionic interactions involving in acid–base reaction. Afterward, they further covalently crosslinked the rubber via the thiol-ene reaction by adding a small amount of trifunctional thiol. By varying the degree of covalent crosslinking, the authors could tune the mechanical properties and the stimuli-responsiveness of the resulting rubber [116]. Recently, Suriano et al. obtained supramolecular networks through
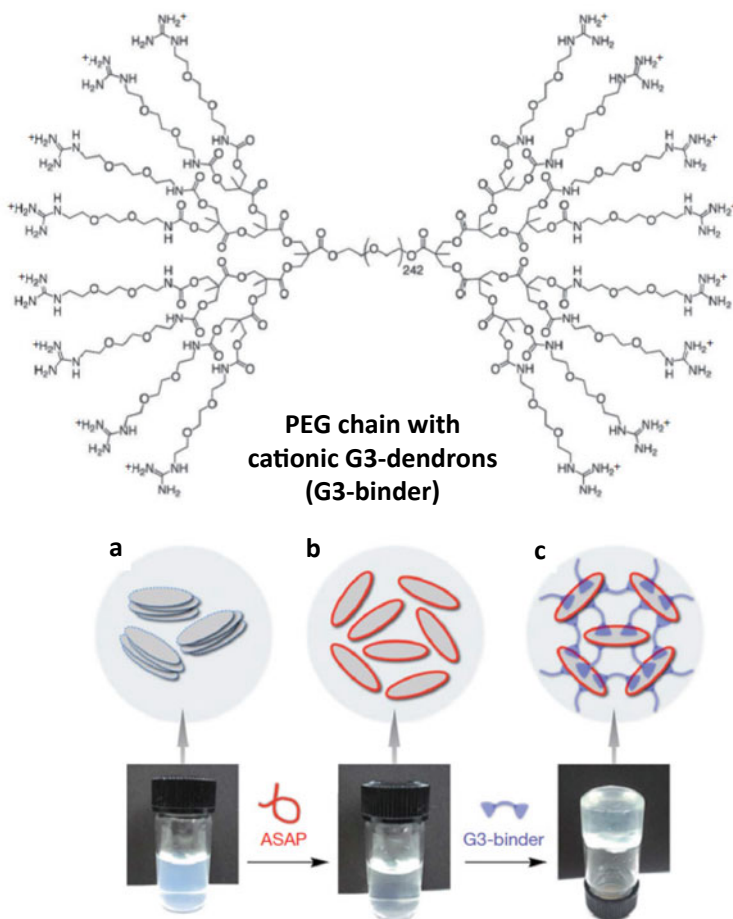
**PEG chain with
cationic G3-dendrons
(G3-binder)**

Fig. 1.13 Top: structure of G3-binder. Bottom: proposed mechanism for hydrogelation: **a** CNSs entangled with one another, **b** dispersing CNSs with ASAP, **c** addition of G3-binder to form electrostatic supramolecular crosslinks. Adopted with permission from the Ref. [112] Copyright (2016) (Royal Society of Chemistry)

implementing acid–base interactions between very viscous carboxylic-terminated and amino-terminated telechelic PDMS oligomers, with different molecular masses (ranging from 900 to 27,000 g/mol). Through analyzing the number of ionic interactions by FTIR analyses, higher values of ionic interactions were achieved in the case of samples with lower molecular mass. A similar same trend was detected for the apparent crosslinking density [117].

The electrostatic interaction between charged polymers also allowed scientists to develop a technique named layer-by-layer (LbL) for designing multilayer films through alternating deposition of polycations and polyanions [118]. In this approach, repeating the electrostatic attachment of polyelectrolytes and washing process leads

to the formation of LbL films onto the solid substrate under precise control. Layers' width, surface charge, morphology, and composition can be adjusted by changing the reaction conditions, the nature of polyelectrolytes, and the number of washing steps [119–122]. LbL approach is specifically appropriate for the immobilization and delivery of biomolecules, such as DNA, antibodies, enzymes, and polysaccharides, as well as bioactive drug molecules [123–126]. For comprehensive understanding of the LbL technique, the reader is directed to some references [127–129] and chapter six of this volume.

1.4   Summary and Future Perspectives

In the recent years, supramolecular ionic networks are broadening the chemistry, physicochemical properties, and applications of conventional polymers. Their self-ordering, guided by electrostatic interactions, provides a simple pathway to highly complex structures. The first advantage of applying electrostatic interactions in the construction of supramolecular assemblies (alone or in combination with other non-covalent interactions) is that the preparation methods are simple and in the second place, numerous molecules and macromolecules are available to be used. In this regard, these structures can be developed from only synthetic materials or from a synthetic material and a natural polymer, such as peptide, protein, and DNA.

The introduction of new cations and anions is extending the synthetic strategies of these networks. As reviewed in this chapter, in terms of synthesis a large number of new supramolecular ionic assemblies have been already designed. However, there is still a high potential for developing innovative ones due to the new types of ions which are being explored driven by the ionic liquid chemistry and the recent progress in precise/controlled polymer chemistry. Placing more emphasis on stimuli-responsive co-assembled networks and nanostructures is identical of great importance and establishes future routes for the design of advanced functional smart nano-objects. In addition, there are still some open questions and challenges remaining. For example, analyzing the ionic assemblies' features and structure at molecular level still is a challenge and additional fundamental research is necessary to check the existing short- and long-range order in the assembly. Also, in order to understand better experimental studies, it is essential to carry out theoretical analyses and modeling of the interaction strength. Once measuring numerous ionic bond strengths and ionic assembly stabilities have been done, then preparing a directory containing value of various ionic interaction strengths would guide scientists to design new assemblies.

From the synthetic perspective, supramolecular ionic assemblies of complex structures (branched, cylindrical, etc.) and well-defined morphologies (nanoparticles, micelles, capsules, etc.) will surely draw growing attention in the field of polymer science. At the same time, material researchers should take into account the costs and sustainability of supramolecular ionic assemblies in their future research directions. Particularly, the assemblies that are developed for different applications should be entirely biocompatible, if not fully biodegradable, and new synthetic routes for

designing polarizable, soft, organic cations and anions may be based on low cost naturally occurring materials, such as amino acids or other functional organic acids and amines. Successively, this strategy will open up the potential commercialization of supramolecular ionic products for everyday life applications.

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