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Supramolecular Assemblies Based on Electrostatic Interactions

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To our families…

Preface

Ionic interactions play an essential role in the self-assembly of functional biological and synthetic systems. Ionic self-assembly, the coupling of two structurally distinct building blocks by electrostatic interactions, has recently become an effective approach to develop new nanostructured chemical objects and materials with interesting and tuneable properties. This ion pairing also plays an important role in the design of supramolecular assemblies, especially in an aqueous environment, where the presence of charges also guarantees adequate solubility. An appropriate molecular structure design of self-assembling building blocks is necessary to obtain tailored properties and even complex functions. Such functions have been already discussed in books and reviews on supramolecular chemistry, also with an emphasis on the underlying binding mechanism.

This volume presents a much-needed update of recent advances and current knowledge in the field of supramolecular assemblies based on electrostatic interactions. The flexibility and simplicity of constructing assemblies are explained via several examples, illustrations, figures, case studies, and historical perspectives. The first two chapters of the book have focused on synthesis aspects and properties of supramolecular ionic networks, including those prepared from small molecules or polymers (or a combination of both), and it is attempted to derive consistent relations between their structure, dynamics, and properties. Within the same context, Chap. 3 discusses the role of electrostatic interaction, purely or in combination with other non-covalent interactions, in the self-assembly of macroions (ranging from 0D to 3D supramolecular structures, e.g., metal-organic cages, dendrimers, biomacromolecules, etc.). Among all macroions, dendrimers have attracted great interest in recent times due to their unique self-assembling properties. Accordingly, a full chapter was included in this book which gives a comprehensive overview of functions, structures, and properties of dendrimers in bulk and in solution (Chap. 4). Moreover, recent developments suggest that electrostatic self-assembly is capable of yielding nano-objects that are well-defined in solution. This emerging field has been fully reviewed in Chap. 5. Layer-by-Layer (LbL) self-assembly is one of the versatile methods used to fabricate multilayered nano-objects, typically under aqueous assembly conditions which involve alternating deposition of multivalent compounds with complementary interactions. In this regard, Chap. 6 provides a broad perspective on the main physicochemical aspects of the fabrication of multilayered nanomaterials through LbL method.

The next two chapters discuss about σ-hole and π-hole interactions where electrostatic contributions are crucial. A deep understanding of noncovalent σ-hole interactions is necessary to advance in many fields, especially in crystal growth and crystal engineering, as illustrated in Chap. 7. Regium-bonding, a new player in supramolecular chemistry, is described in Chap. 8, including examples related to crystal engineering, biological systems, and surface absorption processes.

Nature has created the most beautiful and sophisticated examples of supramolecular assembled systems derived from amphiphilic molecules. Chapter 9 presents the most representative examples (including their design strategy) in electrostatic interaction-based photoresponsive molecular amphiphiles. In the next chapter, self-assembly behavior of amphiphilic salts in solution (mostly based on imidazolium and ammonium) was reviewed as a function of structural features of ionic tectons, emphasizing their implications on the different applications.

Finally, as there is a need for theory and modeling of interaction strength to help experimental studies, the last chapter of the book is dedicated to the topic "Modelling of supramolecular assemblies". It was shown in this chapter, how computational chemistry techniques are particularly helpful for comprehension at the molecular scale of the complex supramolecular polymerization process as well as the relevant properties that final self-assembled architectures could acquire.

This book aims to inspire and guide fellow scientists and students in this field. In this context, the book first merits broad and fast dissemination into the general scientific community especially for the chemists to examine this exciting branch of science to realize its full potential in the new century. Still have a long way to go for a complete understanding, but these volumes demonstrate that rapid and exciting progress is being made.

The Editors express their appreciation to all contributors from different parts of the world that have cooperated in the preparation of this volume. In this context, this international book gives the active reader different perspectives on the subject and encourages him/her to read the entire book.

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Contents

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Abbreviations

1D	One-Dimensional
1N36S	1-naphthol-3,6-disulfonate
3D	Three-Dimensional
AA	All-atom
AA	Amino Acid
AA-FF	All-atom force field
ABnOHRA	Disodium 4-((3-(hydroxymethyl)phenyl)diazenyl)-3-hydroxynaphthalene-2,7-disulfonate
ACQ	Aggregation caused quenching
AEE	Aggregation enhanced emission
AFM	Atomic force microscopy
AIE	Aggregation induced emission
Ala	L-alaninate
ANAC	Abscisic acid-responsive NAC
Ar26	Acid red 26
Ar27	Acid red 27
ASAP	Sodium polyacrylate
ASAXS	Anomalous small-angle X-ray scattering
AT	Anthracene
ATR	Attenuated total reflectance
AuNPs	Gold nanoparticles
Ay38	Acid yellow 38
BETI	Bis[(pentafluoroethyl)sulfonyl]imide
Bis-MPA	2,2-Bis(hydroxymethyl)propionic acid
BS	Benzenesulfonate
BTA	Benzene-1,3,5-tricarboxamide
BTF	Bis-(trifluoromethanesulfonimide)
C_{14}DMAO	Tetradecyldimethylamine oxide
CB7	Cucurbit[7]uril
CBS	Complete basis set
CCSD(T)	Coupled Cluster with single double (triple)

CD	Circular dichroism
CG	Coarse-grained
CG-FF	Coarse-grained force field
CG-MD	Coarse-Grained molecular Dynamic
Ch	Chalcogen atom
ChB	Chalcogen bond
CHI	Chitosan
CiB	Coinage or Regium bond
CLSM	Confocal laser scanning microscopy
CM	Continuum models
CMC	Critical micellization concentration
CNDO	Complete neglect of differential overlap
CNS	Charged clay nanosheets
Col$_h$	Hexagonal columnar mesophase
Col$_r$	Rectangular columnar mesophase
COSMO	Conductor-like screening solvation model
Cryo-TEM	Cryogenic transmission electron microscopy
CSD	Cambridge structural database
CTAB	Cetyltrimethylammonium bromide
CTAT	Cetyl trimethylammonium tosylate
CTC	Chlorotetracycline
Cub$_I$	Micellar cubic mesophase
Cub$_V$	Bicontinuous cubic mesophase
Cys	Cysteine
DFT	Density functional theory
DFT-SAPT	DFT-symmetry-adapted intermolecular perturbation theory
DiCOOH-PEG	Carboxylic acid-telechelic poly(ethylene glycol)s
DLS	Dynamic light scattering
DLVO theory	Derjaguin-Landau-Verwey-Overbeek theory
DMF	N,N-dimethylformamide
DMP[5]A	Dimethoxypillar[5]arene
DMPC	2-dimyristoyl-sn-glycero-3-phosphocholine
DMSO	Dimethylsulfoxide
DNA	Deoxyribonucleic Acid
DOPC	1,2-dioleoyl-*sn*-glycero-3-phosphocholine
DPPC	Dipalmitoyilphosphocoline
DSC	Differential scanning calorimetry
EDTA	Ethylenediaminetetraacetate
ee	Enantiomeric excess
EHT	Extended Hückel theory
ETAB	4-ethyl-4′-(trimethylaminohexyloxy) azobenzene bromide
EWG	Electron withdrawing groups
FeNP	Iron nanoparticles
FF	Force fields
Fmoc	Fluorenylmethyloxycarbonyl

FRET	Fluorescence resonance energy transfer
FTIR	Fourier transform infrared
GAFF	General amber force field
GB	Generalized born
GBSA	Generalized Born and surface area continuum salvation
GFN	Geometries, vibrational Frequencies, and Noncovalent interactions
GGA	Generalized gradient approximation
GLU	Gluconate
$GV_3A_3E_3$	Glycine-Valine-Valine-Valine-Alaine-Alaine-Alaine-Glutamine-Glutamine-Glutamine
Ha	Halogen atom
HA	Hyaluronic acid
HaB	Halogen bond
HB	Hydrogen bonding
HBC	Hexaperi-hexabenzocoronenes
HBS	4-hydroxybenzenesulfonate
HC_1im	1-methylimidazolium
HEWL	Hen egg-white lysozyme
HF	Hartree–Fock
HFB	Hexafluorobenzene
HFIP	Hexafluoroisopropanol
His	Histidine
HMDA	Hexamethylene diamine
HNC	3-hydroxy-2-naphthoate
HOMO	Highest occupied molecular orbital
Ile	Isoleucine
INDO	Intermediate neglect of differential overlap
ITC	Isothermal titration calorimetry
IUPAC	International union of pure and applied chemistry
KS	Kohn–Sham
L-Ala	L-alanine
LbL	Layer-by-Layer
LC	Liquid crystal
LCD	Liquid crystal display
LDA	Local-density approximation
Leu	Leucine
LiTFSI	Lithium bis(trifluoromethylsulphonyl)imide
LJ	Lennard–Jones potential
LLS	Laser light scattering
LP	Lone pair
L-Phe	L-phenylalanine
L-Pro	L-proline
LUMO	Lowest unoccupied molecular orbital
Mb	Myoglobin

MCH	Methylcyclohexane
MCH$^+$	Merocyanine form
MD	Molecular dynamics
MEP	Molecular electrostatic potential
Met	Methionine
MFRM	Melamine-formaldehyde resin microspheres
MM/MD	Classical molecular mechanics and molecular dynamics
MM	Classical molecular mechanics
MOC	Metal organic cage
MOM	Metal organic macrocycle
MOPV	Oligophenylenevinylene
MP2	Møller-Plesset 2
MR	Majority rules
MRI	Magnetic resonance imaging
NCI	Non Covalent Interactions
N$_D$	Nematic Discotic Mesophase
NDC	Naphthalene dicarboxylic acid
NDDO	Neglect of differential diatomic overlap
NDI	Naphthalene diimide
NgB	Noble gas bond
NIR	Near-infrared
NMR	Nuclear magnetic resonance
NOESY	Nuclear overhauser effect spectroscopy
NPA	p-nitrophenylacetate
N-PBIs	*N*-annulated perylene bisimides
NR	Neutron reflectometry
NSA	Naphthalenesulfonate
NT	Naphtalene
NTf$_2$	Bis[(trifluoromethyl)sulfonyl]imide
OPE-TA	Oligo(phenylene ethynylene) tricarboxamide
PA	Poly(acrylate)
PAA	Poly(acrylic acid)
PAH	Poly(allylamine-hydrochloride)
PAMAM	Poly(amidoamine)
PB	Poisson−Boltzmann
PB	Polybutadiene
PBE	Perdew–Burke–Ernzerhof functional
PCM	Polarizable continuum model
PDADMAC	Poly(diallyldimethylammonium chloride)
PDB	Protein data bank
PDI	Perylene-bis(dicarboximide)
PDMAEMA	Poly[2-(N,N-diethylamino)ethyl methacrylate]
PDMS	Poly(dimethylsiloxane)
PEG	Polyethylene glycol
PEI	Hyperbranched polyethyleneimine

PEIMe	Fully methylated hyperbranched polyethyleneimine
PEMs	Polyelectrolyte Multilayers
PFAT	Perfluoroanthracene
PFG-NMR	Pulsed field gradient NMR
PFNT	Perfluoronaphtalene
PGA	Poly(glutamic acid)
PGSE-NMR	Pulsed gradient spin-echo NMR
Phe	Phenylalanine
PLL	Poly(L-lysine)
PM2VP	Poly(N-methyl-2-vinyl pyridinium chloride)
Pn	Pnictogen atom
PnB	Pnictogen bond
POM	Polarized optical microscopy
POM	Polyoxometalate
POPC	Palmitoyl oleyl phosphatidylcholine
POSS	Polyhedral oligomeric silsesquioxane
PPI	Poly(propylene imine)
Pro	L-prolinate
PSA	Polar surface area
PSS	Photostationary state
PSS	Poly(4-styrenesulfonate of sodium)
PTS	p-toluenesulfonate
QM/MM	Quantum mechanics/Molecular mechanics
QM	Quantum mechanics
QTAIM	Quantum theory of atoms in molecules
Rg	Regium atom
RgB	Regium bond
rhB	Rhodamine B
RVFV	Rift valley fever virus
SAIL	Surface active ionic liquids
Sal	Salicilate
SANS:	Small-angle neutron scattering
SaS	Sergeants and soldiers
SASA	Solvent-accessible surface area
SAXS	Small-angle X-ray scattering
SDS	Sodium dodecyl sulfate
SEM	Scanning Electron Microscopy
SFTSV	Severe fever with thrombocytopenia syndrome virus
SLS	Static light scattering
SmA	Smectic A mesophase
SmA^+	Frustrated smectic A mesophase
SmC	Smectic C mesophase
SmCP	Polar smectic C mesophas
SMD	Solvation model based on density
SP	Spiropyrans form

SpB	Spodium bond
SPs	Supramolecular polymers
SQM	Semiempirical quantum mechanical
SSCIS	Spray coating of interacting species
TAEA	Tris(2-aminoethyl)amine
TAPP	Meso-tetrakis-(4-(trimethyl-ammonium) phenyl) porphyrin
TEM	Transmission electron microscopy
TFB	Trifluorobenzene
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
THI	Thermal helix inversion
TMPyP	Meso-tetrakis(4-Nmethyl-pyridinium)porphyrin
TrB	Triel bond
Trp	Tryptophan
TR-SANS	Time-resolved small-angle neutron scattering
TR-SAXS	Time-resolved small-angle X-ray scattering
TS	Tkatchenko–Scheffler approximation
Tt	Tetrel
TtB	Tetrel bond
Tyr	Tyrosine
UPy	2-ureido-4[1H]-pyrimidinone
ur-Py	Ureido-pyrimidone
UV	Ultra-violet
VFT	Vogel-Fulcher-Tamman
WF	Wavefunction
XC	Exchange-correlation
XDM	Becke–Johnson exchange–hole dipole model
XPS	X-ray photoelectron spectroscopy
XRR	X-Ray reflectometry
xTB	Extended tight-binding
ZDO	Zero differential overlap

Nomenclature and Symbols

AC_{60}	Lactic acid-functionalized chiral fullerene
B	Benzene
c	Concentration
$C_1C_{14}im$	1-methyl-3-tetradecylimidazolium
$C_1C_{16}im$	1-methyl-3-hexadecylimidazolium
d	Diameter
D_H	Hydrodynamic Radius
E_a	Activation energy
F	Phenylalanine
G	Dendrimer generation
G4	4th generation
G5	5th generation
G7.5	7.5th generation
G'	Storage moduli
G''	Loss viscous moduli
G_e	Equilibrium elasticity parameter
G_p	Plateau modulus
H_2im	1H-imidazolium
K	Equilibrium constant
M_i	Molar weight between elastically effective interactions
M_n	Number average molecular weight
M_w	Weight average molecular weight
N	Aggregation number
N	Number of bilayers
N	Nematic mesophase
P	Packing parameter
p	PO_4^{2-}
pKa	Acid dissociation constant
R_C	Compensation ratio
r	Radius
R_h	Hydrodynamic radius

R_g	Radius of gyration
$-SO_2-N-SO_2-CF_3$	(trifluoromethane-sulfonyl)imide
$-SO_2-C(CN)_2$	(propylsulfonyl)methanide
$-SO_2-N-CN$	(cyano-propylsulfonyl)imide
T	Temperature
T_g	Glass transition temperature
T_{ln}	Liquid−network transition
T_m	Melting temperature
T_{nl}	Network−liquid transition
Y	Tyrosine
ΔG	Free energy
ΔH	Enthalpy change
ΔS	Entropy change
ε'	Dielectric permittivities
γ_c	Crosslinking density
τ	Relaxation time
ω	Frequency

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 π−π 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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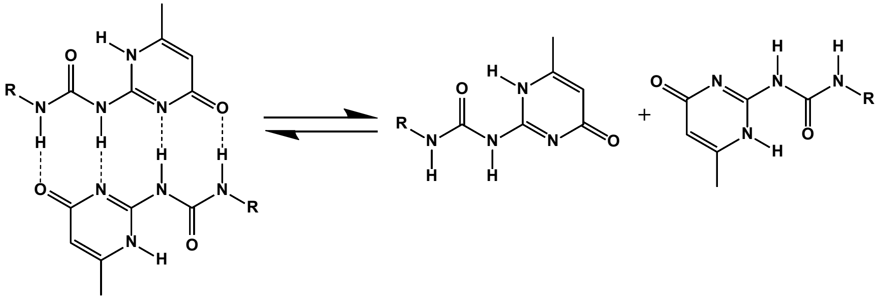
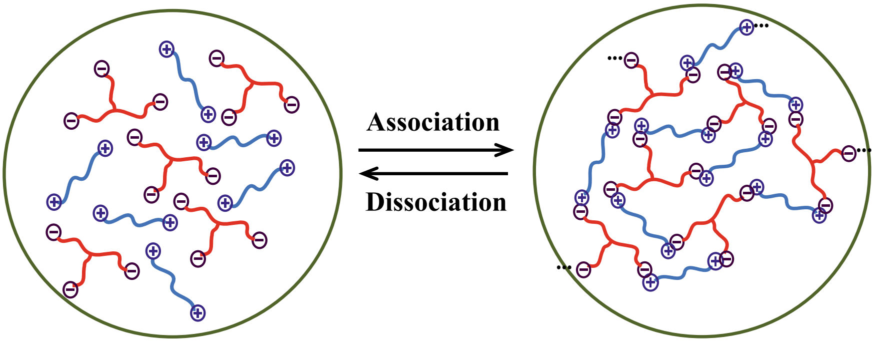


Fig. 1.1 Network structure of the monomer (UPy) units connected by reversible hydrogen bonds. The UPy units form four hydrogen bonds to each other (dotted lines)

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

Reused with permission from Ref. [22] Copyright (2013) (Wiley) 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 6×10^7 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).

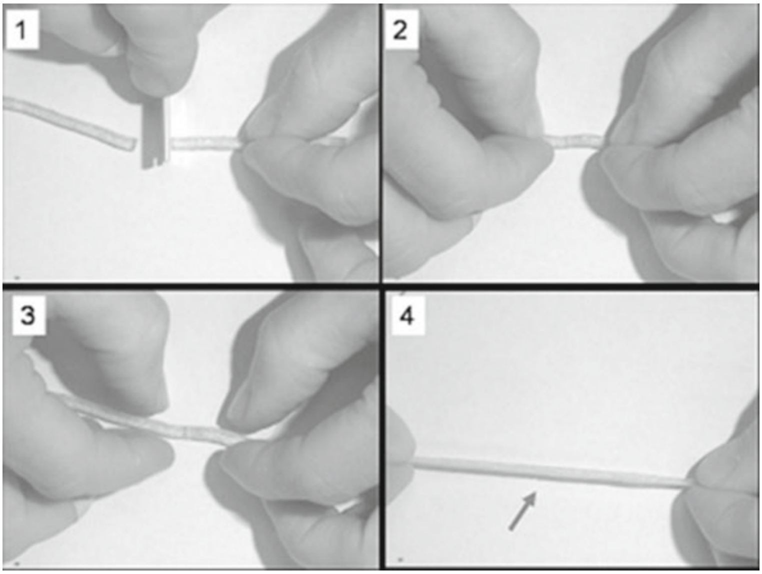


Fig. 1.2 Self-healing supramolecular elastomer developed by Leibler et al. Reproduced with permission from the Ref. [28] Copyright (2015) (Wiley)

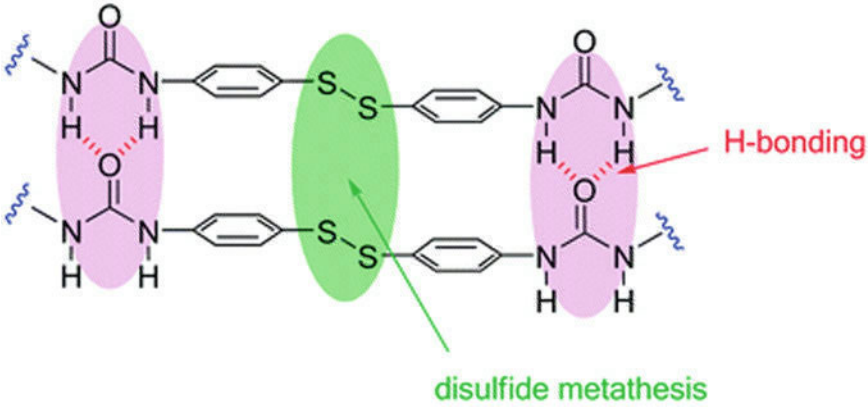


Fig. 1.3 Proposed bonds involved in the self-healing material developed by Odriozola et al. Reproduced with permission from the Ref. [28] Copyright (2014) (Royal Society of Chemistry)

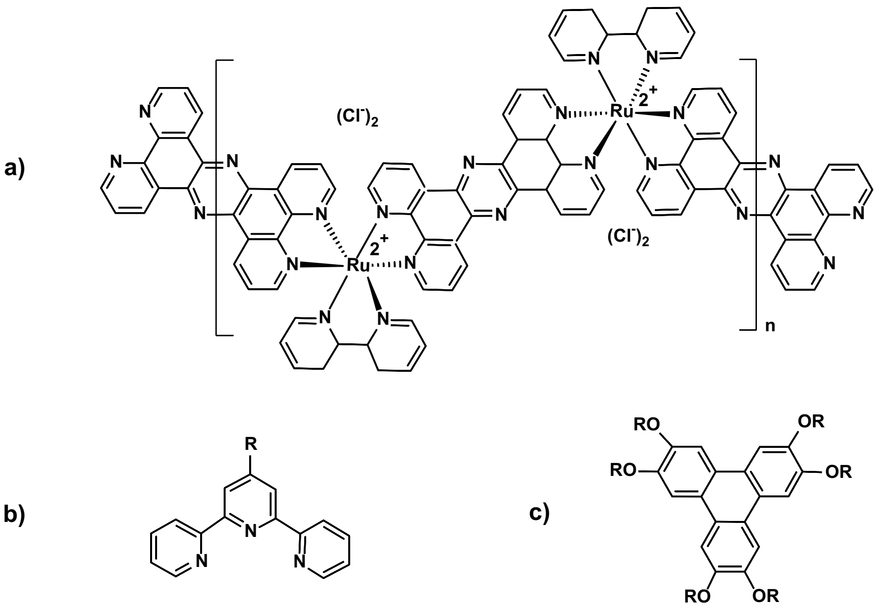


Fig. 1.4 **a** An example of Ruthenium(II) coordination polymer complex, **b** a model structure of terpyridine ligand and **c** molecular structure of triphenylene

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].

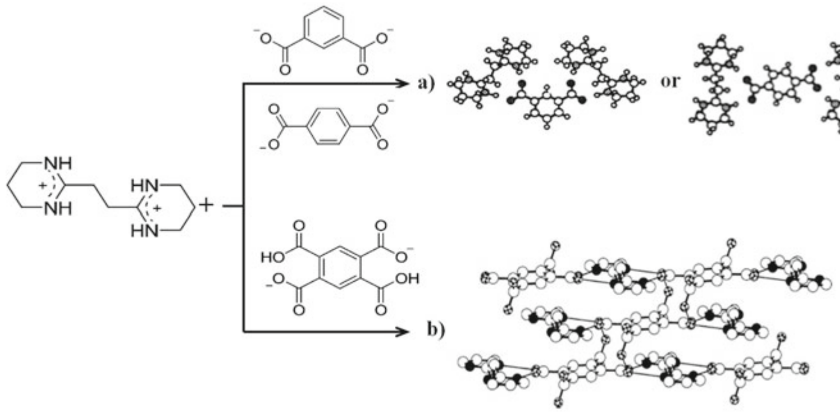


Fig. 1.5 Chemical structures of dicationic cyclic amidinium, phthalate dianions, pyromellitate dianion and X-ray structures of the resulting **a** linear or **b** 2-D network assemblies. Adapted with permissions from the references [61, 62] Copyright (1994, 2001) (Royal Society of Chemistry, Elsevier), 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 interactions 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_2TPP^{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

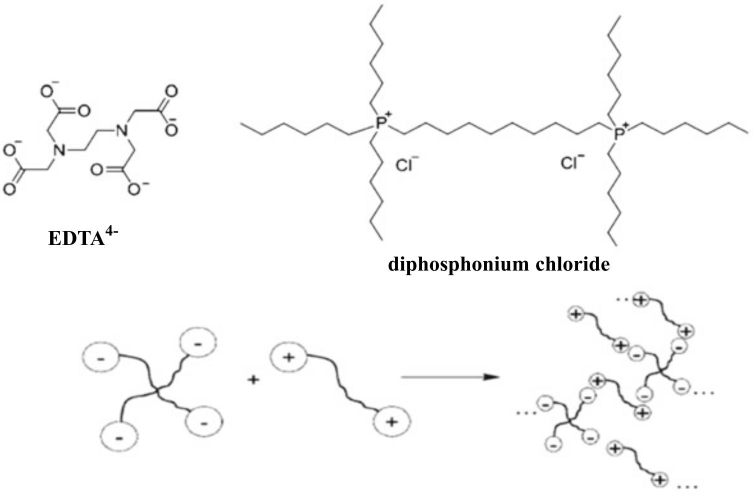


Fig. 1.6 Formation of a supramolecular ionic network reported by Grinstaff et al. (up): chemical structures involved; (down): schematic diagram of network formation. Reproduced with permission from Ref. [22] Copyright (2013) (Wiley)

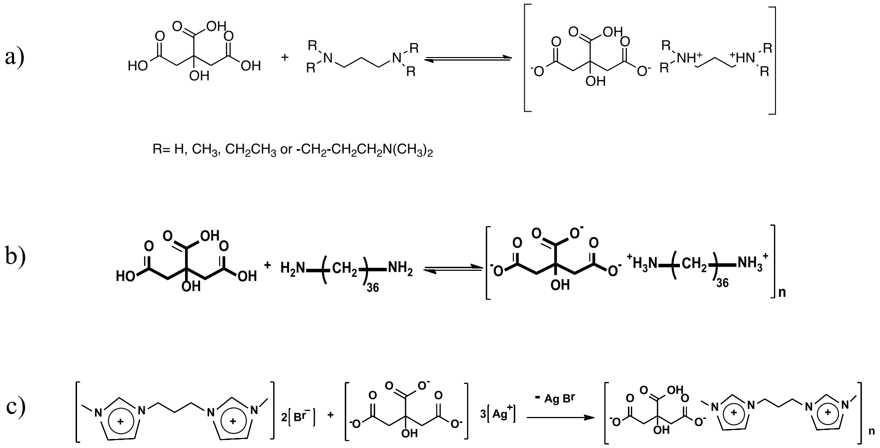


Fig. 1.7 Proposed reaction pathway for the synthesis of supramolecular ionic networks based on citric acid and **a** commercially available di- or trifunctional amines **b** a fully renewable C36 biobased diamine (Priamine 1074) and **c** geminal dicationic ionic liquids. Reproduced with permissions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