Recent Advances in Metal-Containing Polymer Hydrogels

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Abstract

Metal-containing polymer hydrogels have attracted increasing interest in recent years due to their outstanding properties such as biocompatibility, recoverability, self-healing, and/or redox activity. In this short review, methods for the preparation of metal-containing polymer hydrogels are introduced and an overview of these hydrogels with various functionalities is given. It is hoped that this short update can stimulate innovative ideas to promote the research of metal-containing hydrogels in the communities.

Graphical abstract

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Conflict of Interest: The authors declare no conflict of interest.
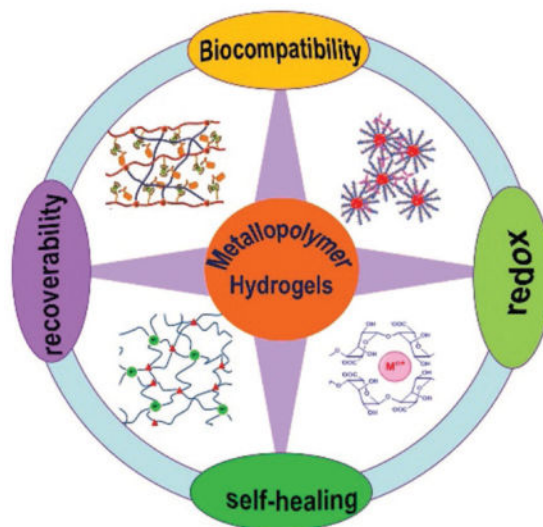
Keywords

crosslinked; hydrogels; metal-containing polymers; molecular interactions

1. Introduction

Conceptually, a natural or synthetic hydrogel formed by chemical and/or physical crosslinking is a hydrophilic polymeric network with a high ratio (volume or weight) of water to dry gel. Owing to many of outstanding properties such as biocompatibility, tunable mechanical property, and stimuli responsiveness, polymer hydrogels are extensively used in tissue engineering, protein separation, drug delivery, sewage treatment, artificial extracellular materials, etc.[1] Recently, considerable interest has arisen in the preparation and application of metal-containing polymers due to the incorporation of both organic and inorganic components.[2] They combine processing advantages of soft polymers and unique functions provided by hard metal centers. Basically, organic polymers provide flexibility, solubility, and processability, while incorporation of metal elements endows multiple functionalities including redox activity, catalytic, magnetic, responsive, and electronic properties.[3] Therefore, metal-containing polymers with unique and versatile properties should be one of the ideal materials for manufacturing functional hydrogels.

In general, according to the nature of interactions involved in their formation, metal-containing polymer hydrogels can be classified as crosslinked hydrogels via metal coordination,[4] covalently crosslinked hydrogels,[5] and hybrid crosslinked hydrogels.[6] Currently, the most extensively studied metal-containing hydrogels are crosslinked hydrogels via coordination that are held together by metal cations. However, the covalently crosslinked metal-containing hydrogels, especially metallocene-containing polymer hydrogels, are far less studied, partly because of the cytotoxicity of metals and the difficulty in incorporating metal centers into macromolecular networks. Up to now, few review articles have comprehensively summarized metal-containing polymer hydrogels. An earlier review

only introduced poly(ferrocenylsilane) (PFS) hydrogels as redox-responsive materials.[5] In this review, we mainly discuss the preparation and application of metal-containing hydrogels developed in recent years. The metal-containing supramolecular hydrogels will not be covered as a stand-alone section here, and readers can find them in relevant reviews.[4,7] Moreover, we will give perspectives on the future development of metal-containing hydrogels.

2. Crosslinked Hydrogels via Metal Coordination

Coordination interactions between metal ions and functional groups in polymer chains are frequently used as crosslinking junctions to fabricate metal-containing hydrogels. Coordination is usually a special chemical bond in which one atom typically supplies electrons, different from a traditional covalent bond in which each atom supplies electrons. Metal coordination resulting from Lewis acid–base interactions is stronger than most noncovalent interactions, but weaker than prototypical covalent bonding interactions (e.g., C–C, C–O, etc.). Thus, hydrogels, like classic Ca-alginate gels,[1f] prepared by metal coordination might possess properties of either physical or chemical gels in different situations. Based on coordination interactions, the formed metal-containing polymer hydrogels exhibited many excellent properties such as biocompatibility, recoverability, self-healing, and redox activity.[3d,8]

Several metal-coordination hydrogels made from polyvalent metal ions and polysaccharide (alginate) have been reported.[9] Anionic alginate solution can generate hydrogels by using metal cations (Fe^{3+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) as crosslinking agents, which can facilitate coordination with carboxylate groups of alginate. It should be pointed out that the G (guluronic acid) blocks in various alginate chains establish crosslinks through metal coordination, leading to a metal-alginate hydrogel (Figure 1).

Machida-Sano et al. reported a biocompatible metal-coordination hydrogel prepared from ferric ion and alginate, which can be used for cell support.[9a] Ostrowski and co-workers showed that light-responsive hydrogels can be prepared by the coordination of iron(III) and ionic polysaccharides. The physical state of these hydrogels can be changed under light stimuli due to the redox activity of polyvalent metal ions. This kind of light-responsive hydrogels has potential in the area of biomedicine and tissue engineering.[9b,c] Similar iron(III) cross-linked alginate hydrogels were also reported by Melman and co-workers.[9d] Recently, Zhang and co-workers reported metal ion cross-linked alginate hydrogels that can be served as shapeable and versatile templates for insitu metal–organic framework (MOF) growth, and the shapes of hydrogels were easily inherited by their corresponding MOF–alginate composites.[10]

A polymer hydrogel was fabricated by the complexation of ferric ion (Fe^{3+}) and poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)).[11] Metal coordination between Fe^{3+} and carboxyl groups of P(AAm-co-AAc) generated physical crosslinks in the gel matrix, and this physical hydrogel possesses high stiffness and toughness, fatigue resistance, and stimuli-triggered healing along with shape memory and processing abilities.

New iron-containing polymer hydrogels were prepared by means of coordination interactions between Fe^{3+} and carboxylates in an amphiphilic diblock copolymer poly[(N-isopropylacryl-amide-co-2-nitrobenzyl acrylate)-block-(N, N-dimethylacrylamide-co-acrylic acid)] (Figure 2).[12] The obtained hydrogels exhibited sol-gel transition behaviors by UV irradiation, multidentate ligand (EDTA), and redox agent ($Na_2S_2O_4$).

In addition, coordination involving other metal ions and anionic groups can also be utilized to initiate the gelation process. For instance, Andzelm and co-workers reported that hydrogels can be produced by adding divalent or trivalent cations (Ca^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}) into a dispersion of cellulose nanofibrils.[13] They also exploited the ionic interactions of metal ions with carboxylate groups to initiate the gelation process. The hydrogel storage moduli were related to valency of the metal ions, their binding strength with carboxylate groups on the nanofibrils, and the choice of cations.

Wegner et al. reported a redox-responsive hydrogel made from 4-arm histidine-modified poly(ethylene glycol) (4A-PEG-His) with cobalt ions as a crosslinker in water (Figure 3).[14] With a simple oxidation step from Co^{2+} to Co^{3+}, the physical state of the prepared hydrogels can be changed from self-healing viscoelastic liquids to stable elastic solids (Figure 3A). Moreover, different ratios of cobalt ions to histidine end-group (e.g., 1:2 and 1:3) can lead to different connectivity of polymer networks in the cobalt crosslinked hydrogels (Figure 3B). Using the same 4A-PEG-His, Messersmith and co-workers developed novel mussel-inspired metal coordination hydrogels with Zn^{2+}, Cu^{2+}, Co^{2+}, or Ni^{2+} as a crosslinker.[15]

Based on metal coordination, Nitschke and co-workers prepared a new class of metal–organic cage-cross-linked polymeric hydrogels through the self-assembly of formylpyridine functionalized PEG in the presence of Fe^{2+} (Figure 4).[16] Two distinct internal phases in the hydrogel were formed by selective encapsulation of guest molecules within the cages. Depending on their aptitude for encapsulation within the cages, the two internal phases present in the gels can allow small molecules to be released at different rates and in response to competing guests.

3. Covalently Crosslinked Hydrogels

Over the past six decades, a great number of metal-containing polymers have been synthesized either by integrating metal centers into the main chain or by attaching them as pendant groups at the side chain, and the linkages that couple the metal centers can be strongly covalent bonded or reversibly and dynamically coordinated.[17] These polymers can be directly utilized to prepare metal-containing hydrogels taking advantage of prototypical covalent bond as crosslinking points (metals do not participate the crosslinking).

As a star member of the metallocene family, ferrocene can be integrated into the main chain to fabricate metal-containing polymer hydrogels.[5] The first ferrocene-containing polymer hydrogel was reported by Hempenius et al..[18] Two different kinds of poly(ferrocenylsilane) polyion hydrogels, containing positively and negatively charged side groups, respectively, were manufactured by covalent cross-linking methods. The hydrogels owed a high water swelling ratio and displayed reversible redox responsive properties. In 2010, Hempenius and

co-workers developed a redox responsive metal-containing hydrogel by a thiol–Michael addition click reaction,[19] using poly(ferrocenylsilane) as a redox-responsive component and poly(ethylene glycol) dithiol as a crosslinker (Figure 5). Recently, they further developed a new class of redox-active hydrogels of anionic poly(ferrocenylsilane) polyelectrolytes by a copper-free azide-alkyne Huisgen cycloaddition reaction. These hydrogels were used for the in situ formation of rather well-defined palladium nanoparticles.[20]

Cationic cobaltocenium-containing polymers have been recently gaining a lot of attention.[21] Taking advantage of antimicrobial activities and hydrophilicity of cationic cobaltocenium,[8b,15,22] Tang and co-workers recently constructed novel cationic cobaltocenium-containing polymer hydrogels (PCoCl-Gel) (Figure 6). They introduced the cationic cobaltocenium moiety into polymeric networks by free radical polymerization of cobaltocenium methacrylate with a PEG functionalized crosslinker.[23] These hydrogels easily absorbed β-lactam antibiotics because of the ability of cobaltocenium to bind anionic antibiotics, which can be applied to treat antibiotic-contaminated water. Moreover, these cationic hydrogels can inhibit the growth of different bacteria, including drug-resistant strains.

Different from metallocene-containing hydrogels, Zhou et al. reported Ru(II)(Tpy)$_2$-functionalized polymer hydrogels with metal centers linked by coordination interactions.[24] Two synthetic routes were developed to prepare Ru(II)(Tpy)$_2$-functionalized polymer hydrogels. The first one is the direct gelation by copolymerization of acrylamide (as a hydrophilic component) and Ru(II)(Tpy)$_2$ (as the functional group). The second one is that the terpyridine-containing hydrogel was first prepared and then post-functionalized by coordination between Ru(III)(Tpy)Cl$_3$ and terpyridine groups (Figure 7). According to the latter method, Sahiner et al. prepared metal-containing poly(1-vinyl imidazole) hydrogels as a reaction container for catalysis of various organic reactions.[25] Electrostatic interactions between metal complex cations and anionic functional groups of polymer chains can also be used to create metal-containing hydrogels.[26] A typical example is a metal-containing hydrogel prepared by incorporation of positive [Ir(2- phenylpyrine)$_2$ (4,4′-dimethyl-2,2′-bipyridine]Cl into negative poly(2-acrylamido-2-methylpropane sulfonic acid sodium) hydrogel via electrostatic interaction, which exhibited stable phosphorescence (Figure 8).[27]

4. Hybrid Crosslinked Hydrogels

From a practical point of view in many situations, metal-containing polymer hydrogels should have good mechanical properties. Thus, a combination of ionic interactions and other interactions such as covalent and coordination bonds as crosslinking means is preferred to prepare metal-containing hybrid crosslinked hydrogels with enhanced performance. An example of a metal-containing hydrogel formed by ionic and covalent interactions was given by Xie and co-workers.[28] An iron-containing hydrogel was prepared by one-pot free radical polymerization of acrylic acid (AA) with N, N′-methylenebisacrylamide as the covalent crosslinker and Fe(NO$_3$)$_3$ as the ionic crosslinker. Many reversible crosslinks are formed as a result of coordination interactions between Fe^{3+} ions and carboxyl groups of

PAA within the sparse, covalently crosslinked network (Figure 9a). It is the unique network structure that makes the PAA hydrogel to have high toughness and stretchability (Figure 9b).

Meyer and co-workers reported a dually crosslinked iron-containing electroplastic elastomer hydrogels prepared with poly(ethylene glycol) diacrylate as a chemical crosslinker and Fe^{3+} as a physical crosslinker.[29] These hydrogels can be reversibly switched between hard and soft states while maintaining a 3D shape by sequential switch of oxidative and reductive potentials. Later, the same group reported another dually cross-linked copper-containing electroplastic elastomer hydrogels, which undergo changes in mechanical properties in response to both chemical and electrochemical stimuli.[30]

Recently, Wang and co-workers reported a dual physically crosslinked (DPC) hydrogel by mixing poly(acrylamide-co-acrylic acid), clay nanosheets, and iron (III) chloride hexahydrate.[31] The primary crosslinking junctions were introduced by coordination interactions between Fe^{3+} and carboxylate groups in P(AM-co-AA) polymer chains. Then, the clay nanosheets were induced to form the secondary crosslinking points through the interaction of hydrogen bonds with P(AM-co-AA) chains. The optimal DPC hydrogels possessed superior mechanical properties such as high tensile strength ($\approx$3.5 MPa), large elongation ($\approx$21 times), remarkable toughness ($\approx$49 MJ m^{-3}), and good self-recoverability.

Gohy and co-workers first synthesized a poly(triethyleneglycol methylether methacrylate)-*b*-poly-styrene block copolymer (PTEGMA-*b*-PS) that consisted of a hydrophobic PS block and a soluble PTEGMA block containing terpyridine repeating units. Then, a Ni-containing hybrid crosslinked PTEGMA-*b*-PS hydrogel was obtained through the hydrophobic interaction of PS blocks and the coordination interactions between the terpyridine groups of PTEGMA and the Ni(II) ions. The moduli of PTEGMA-*b*-PS hydrogel were much higher than those of PTEGMA homopolymer hydrogel, which has only the coordination interaction.[32]

To further improve the mechanical strength of hydrogels, double network (DN) or interpenetrating network (IPN) polymer structures have also been employed for fabricating metal-containing hydrogels in recent years.[33] Using the DN concept, Suo and coworkers synthesized extremely stretch-able and tough hydrogels by mixing two types of crosslinked polymers:[9e] one polymer network is calcium crosslinked alginate; the other is covalently crosslinked polyacrylamide with *N, N*-methylenebisacrylamide as the crosslinker. The calcium-containing hydrogels, with a water content of 90%, can be stretched beyond 20 times of their initial length, and have fracture energies of 9000 J m^{-2}.

Zheng and co-workers first used an agar gel as the first physical network and a copolymer of acrylamide and acrylic acid (PAMAAc) gel as the second chemical–physical network to form an Agar/PAMAAc DN hydrogel (Figure 10).[34] Then, a new type of Agar/PAMAAc-Fe^{3+} DN hydrogels was obtained by introducing Fe^{3+} ions into the second network to form strong coordination interactions. These DN hydrogels possess high mechanical properties, fast self-recovery (50% toughness recovery after 1 min of resting), and good fatigue resistance.

Waite and co-workers prepared metal-containing IPN hydrogels with rate-dependent stiffness and recovery by incorporating the coordination-based hydrogels into poly(hydroxyethyl acrylamide)-based covalent scaffolds.[35] The coordination-based hydrogels were fabricated by the complexation of trivalent metal cations (In^{3+}, Fe^{3+}, and Al^{3+}) and 4-arm PEG star polymers modified with 3-hydroxy-4-pyridinone.

5. Conclusions and Perspective

In summary, different molecular interactions (metal coordination, prototypical covalent bonding, and a hybrid of both) are used to introduce crosslinking for the formation of metal-containing hydrogels. The presence of metal centers as an integral part of the matrix of a polymer hydrogel can provide a wide range of properties pertained to these soft materials. Many recent examples of preparation and applications of metal-containing polymer hydrogels may underscore significant advances in the future.

In general, the ionic crosslinks, especially metal coordination, could result in the formation of dynamic and responsive metal-containing polymer hydrogels. It is critical to not only achieve an optimization on the strength of these ionic interactions, but also maintain dynamic and responsive properties. Although the covalent crosslinks can be used to obtain metal-containing polymer hydro-gels, the main challenges are to develop novel monomers containing metal centers that provide more opportunities for fundamental physiochemical properties as well as real applications. Nevertheless, the hybrid crosslinks with coordination and covalent interactions are probably more preferred to fabricate metal-containing hydrogels, such as DN and IPN gels, with high strength and responsive properties. However, shortcomings of these hydrogels lie in their complexity in terms of preparation processes compared to single network metal-containing hydrogels with either a metal-coordination or prototypical covalent crosslink. We hope that more creative ideas will be stimulated to promote research on metal-containing hydrogels with various functionalities.

Acknowledgments

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Biographies

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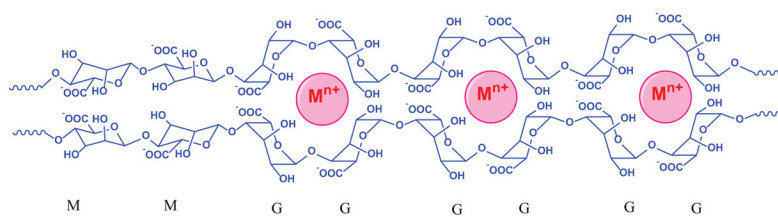
Figure 1.
Illustration of cross-linking of alginate by M^{n+} metal cations. An alginate chain contains mannuronic acid (M unit) and guluronic acid (G unit). Reproduced with permission.[9e] Copyright 2012, Nature Publishing Group.
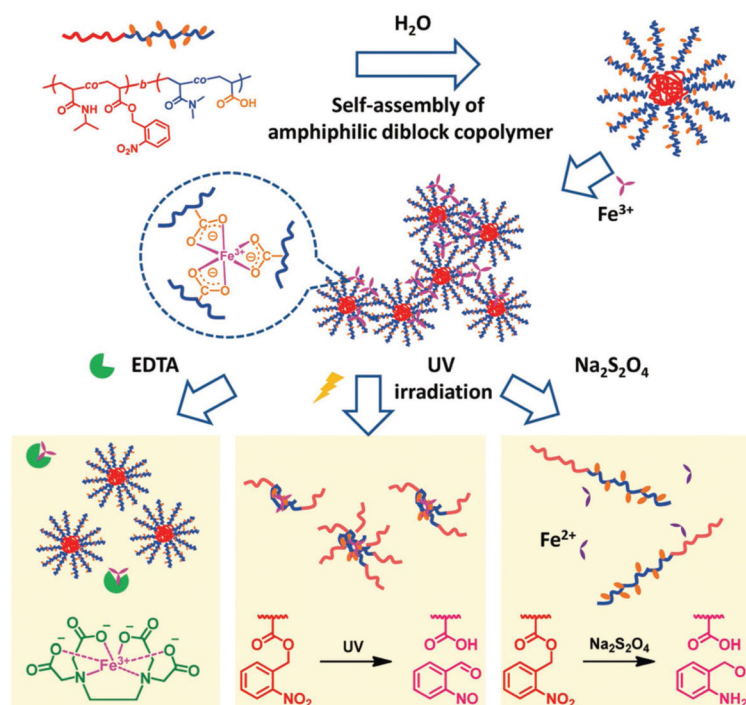
Figure 2.
Gelation by micelles and complexation of Fe^{3+} and polymer chains, and sol-gel transition triggered by EDTA, UV irradiation, and $Na_2S_2O_4$. Reproduced with permission.[12] Copyright 2016, Royal Society of Chemistry.
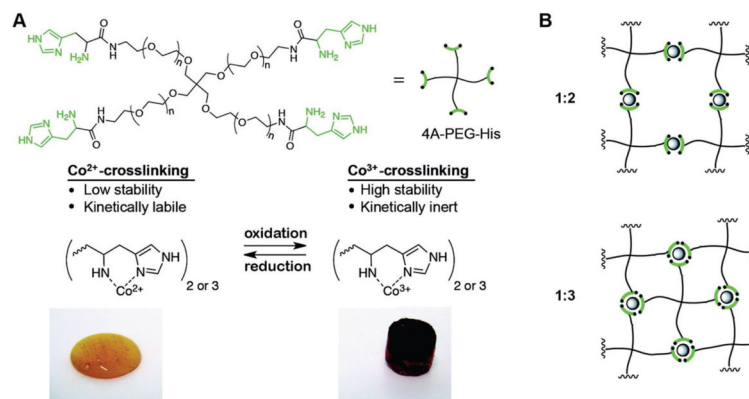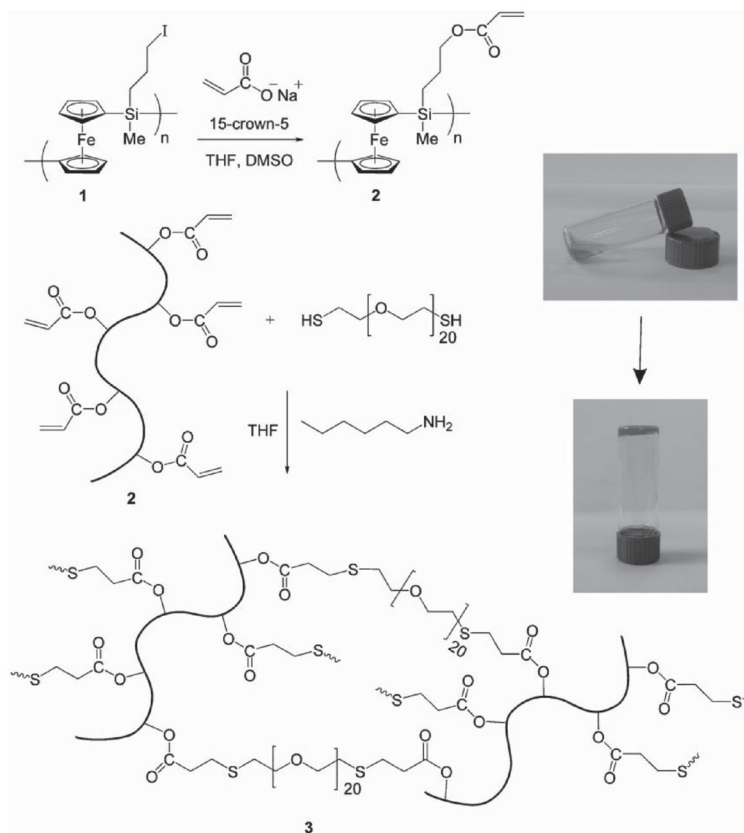
Figure 3.
A) Cross-linking of the 4A-PEG-His with Co^{2+} or Co^{3+} resulted in hydrogels with very different physical properties; B) different ratios of cobalt ions to histidine end-group ratios (1:2 and 1:3) led to different hydrogel connectivity. Reproduced with permission.[14] Copyright 2016, American Chemical Society.
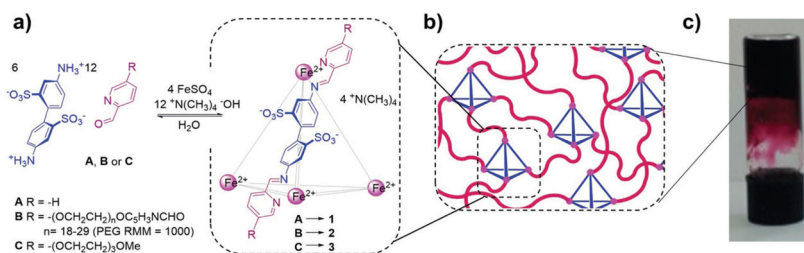
Figure 4.
Metal–organic cage cross-linked hydrogel formation: a) synthesis of cages 1–3 using aldehydes A–C, and b) a schematic view of the structure of cage-cross-linked gel. c) A photograph showing an inverted vial containing a 15 wt % hydrogel formed by cage 2. Reproduced with permission.[16] Copyright 2015, American Chemical Society.
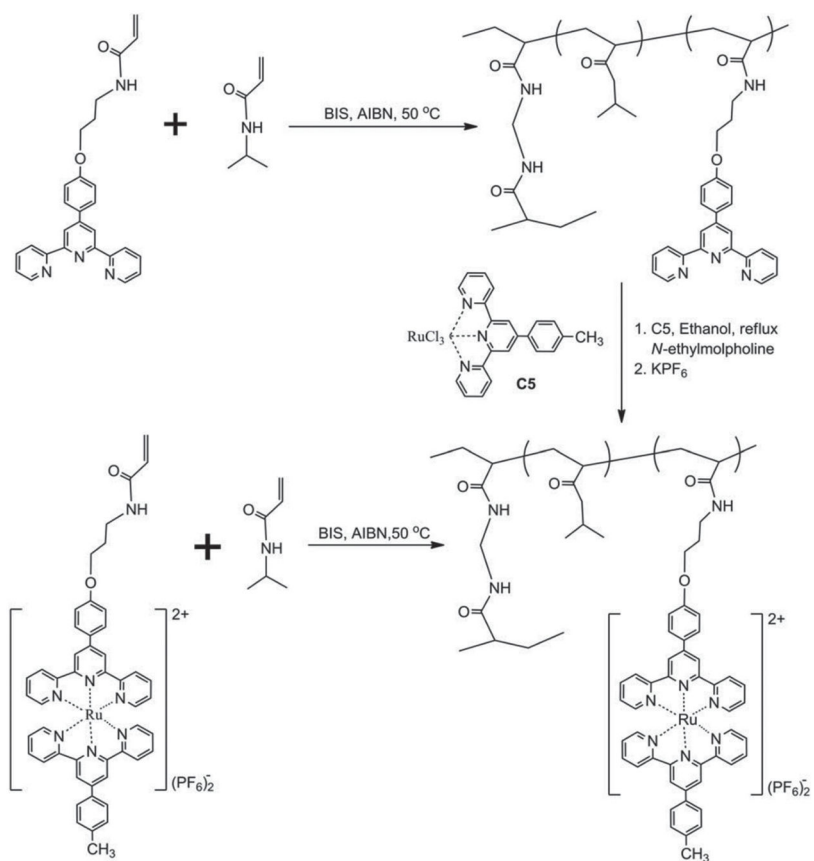
Figure 5.
Synthesis of PFS-PEG-based hydrogel and photographs of the gel formation. Reproduced with permission.[19] Copyright 2010, Wiley-VCH.
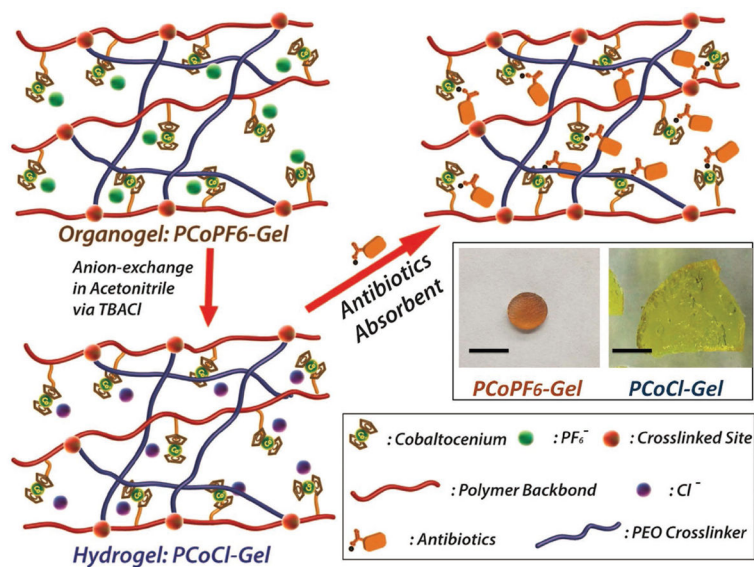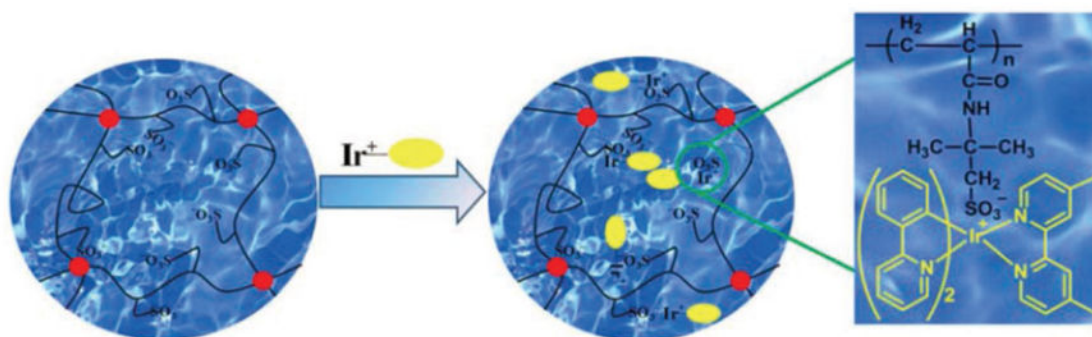
Figure 6.
Illustration of anion-paired (Cl⁻, purple spheres; PF₆⁻, green spheres; and antibiotics) cobaltocenium-containing organogels and hydrogels. Inserted: optical images of two representative gels (Scale Bar: 1 cm). Reproduced with permission.[23] Copyright 2015, Springer Nature.
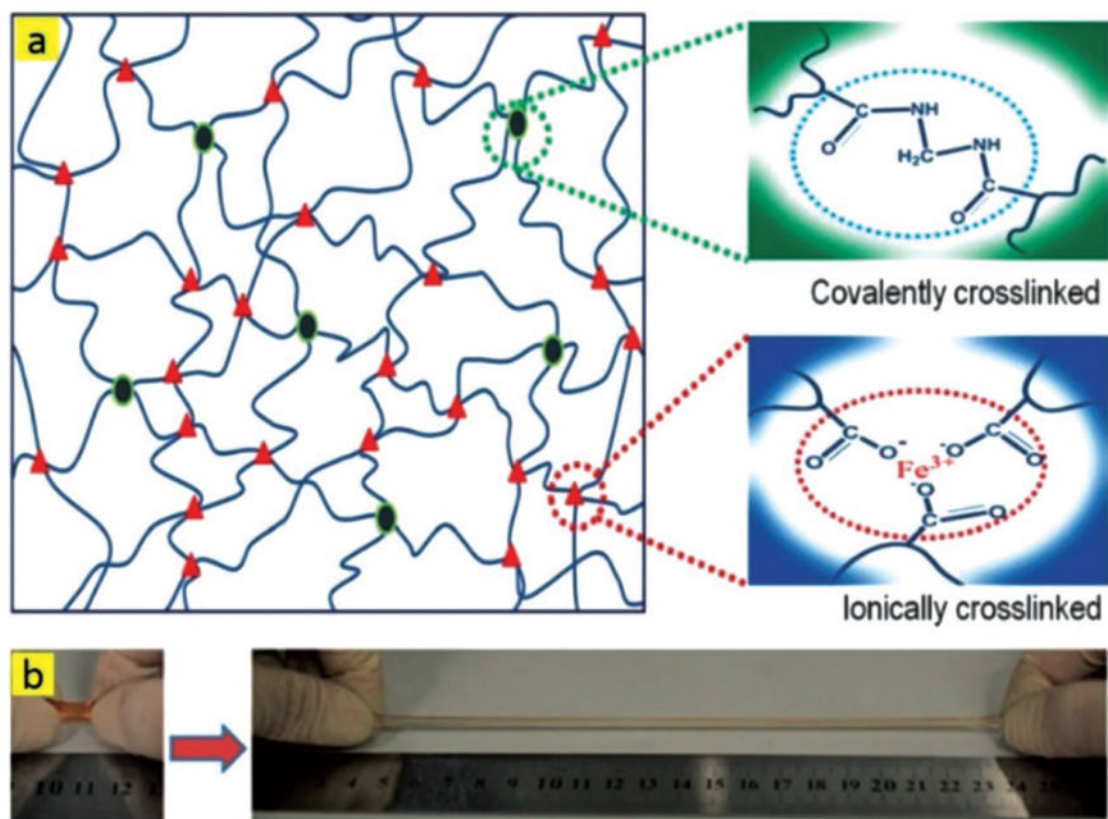
Figure 7.
A synthetic route for Ru (II) (Tpy)$_2$ -functionalized hydrogels. Reproduced with permission.[24] Copyright 2015, Wiley-VCH.
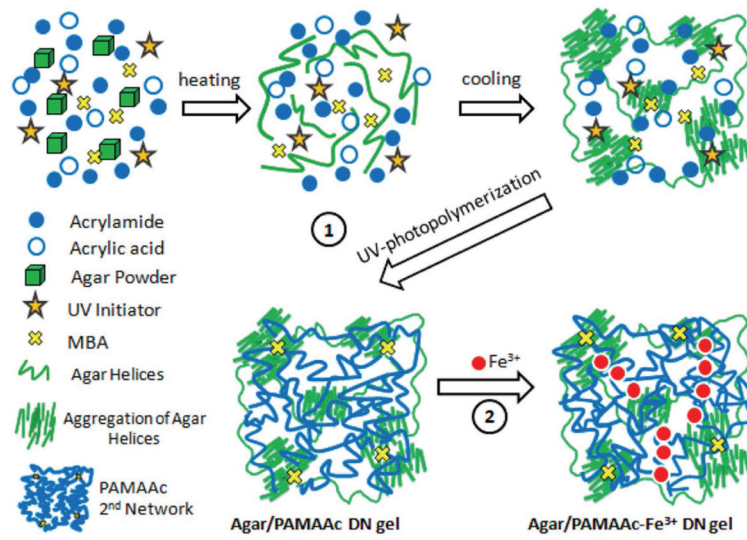
Figure 8.
A schematic diagram of electrostatic interaction between the PNaAMPS hydrogel and [Ir(ppy)$_2$(dmbpy)]Cl (red circle: crosslinking point, blank line: polymer network, yellow ellipse: ([Ir(ppy)$_2$(dmbpy)]Cl). Reproduced with permission.[27] Copyright 2012, Wiley-VCH.

Figure 9.
a) Iron-containing PAA hydrogels by electrostatic and covalent interactions; and b)
photographs of PAA hydrogels with high stretchability. Reproduced with permission.[28]
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Figure 10.
Synthesis of Agar/PAMAAc-Fe^{3+} DN gels. Reproduced with permission.[34] Copyright 2016, American Chemical Society.