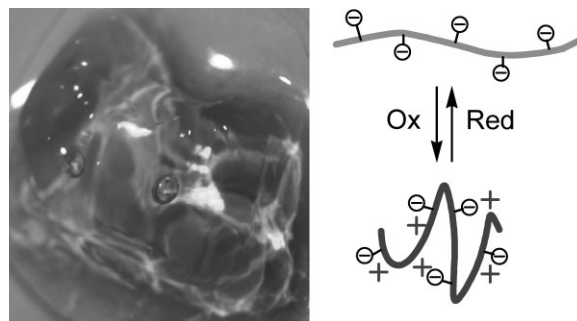


Poly(ferrocenylsilane) Gels and Hydrogels with Redox-Controlled Actuation

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G. Julius Vancso*

This concise paper discusses poly(ferrocenylsilane) (PFS)-based organometallic gels and hydrogels as a novel class of redox-responsive materials. First, the use of silicon-bridged spirocyclic [1]ferrocenophane crosslinkers for creating PFS networks swellable in organic solvents is described. Optical properties of PFS composite colloidal crystal films, composed of monodisperse silica spheres embedded in such PFS networks, are shown to be influenced by solvent swelling or redox chemistry, allowing the use of these composites in photonic crystal full-color displays. The synthesis of networks composed of water-soluble PFS polyanions or polycations is discussed. In response to redox stimuli, a polyanionic PFS-hydrogel exerted a pressure, which could render it useful as an actuator.



Introduction

Networks composed of polymer chains, linked together by covalent or noncovalent bonds, form gels when immersed in their solvent. Large amounts of solvent may be absorbed by the network, depending on polymer chain characteristics, crosslink density, the presence of ionic charges, and the polymer–solvent interaction parameter χ .^[1] Variations in environmental conditions may induce large two-dimensional (bending) or three-dimensional (volume) changes in gels, which may be exploited for a variety of applications. Stimulus-responsive gels^[2] are attracting much attention due to their potential use in controlled

release systems^[3] where drugs or cosmetics can be released upon receiving a specific stimulus, or as actuators, artificial muscles or valves.^[4,5] Typical stimuli used to date include changes in temperature,^[6] pH,^[7] ionic strength,^[8] electric field strength,^[9] light intensity,^[2d] and magnetic field strength. A variety of magnetic field-sensitive flexible and rigid polymer composites have recently been developed.^[10] These composites include the sub-class of magnetic field-sensitive, or magnetostrictive polymer gels.^[2d] These gels consist of nano- or micrometer-sized magnetic particles embedded in a crosslinked polymer matrix, containing a significant amount of swelling liquid. The magnetic components can be aligned which allows one to induce deformation and trigger a range of motions.^[10] Alignment has also been shown to cause a stiffening and strengthening of the magnetostrictive gels, which provides a basis for their use as actuators.^[11] Microgel particles with multiple sensitivities including pH-, temperature-, and magnetic field-responsiveness are of interest for biomedical and bioengineering applications due to their facile magnetic separation.^[12] In addition, due to their responsiveness to both magnetic field and temperature, thermoresponsive magnetic microspheres have potential use as a targeted

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drug delivery system. After loading a specific drug, the particles may be guided to the site of choice by an external magnetic field and subsequently the drugs might be released, using temperature as a trigger.^[12]

Gels responsive to redox stimuli are relatively scarce.^[13] Redox responses in susceptible gels may be induced chemically or electrochemically. In the first case, the presence of e.g., an oxidant may trigger responses that would allow the gel to be used as a sensor. Electrochemically applied redox stimuli offer several key advantages over the classic stimuli as they may allow fast and reversible switching between oxidized and reduced states and can be applied externally. The electrochemical processes and hence the induced responses can be controlled by computer. In addition, due to access to nanofabricated electrodes or metallic lines, redox-responsive systems can be addressed at the nanoscale, which makes their integration in devices feasible.

Redox-responsive polymer gels belong to the category of electroactive polymers (EAPs). EAPs are flexible, responsive materials that are capable of converting electrical energy into mechanical energy, thus imparting a force and/or motion.^[14] EAPs are commonly divided into two general categories on the basis of their physical state or actuation mechanism. Ionic (or wet) EAPs include ionic polymer-metal composites (IPMCs) and conjugated polymers and they rely on ion and solvent transport to induce volume changes. Electronic (or dry) EAPs, where actuation is based on Coulombic forces, encompass electrostrictive polymer actuators and dielectric elastomers. A major difference between the ionic and the electronic EAPs is that ionic EAPs, among which are the redox-active gels, require low voltages (typically 1–3 V) to operate whereas the electronic EAPs actuate at high voltages (100–1 000 V). Electronic EAPs show short response times, typically in the milliseconds,^[15] while response times for ionic EAPs are on the order of 1 s for films and fibers up to several micrometer thick, as volume change depends on mass transport.^[14a] The actuator characteristics of the various EAPs have been thoroughly described by Smela^[14a] and by Spontak and coworkers.^[14b] While conjugated polymers such as polypyrrole and polyaniline are well-established as redox-mediated actuators,^[14,16] there is a continuous need for novel redox-responsive materials with increased stability, reversibility, tunability, decreased driving voltages, etc. This concise paper is concerned with stimulus-responsive and actuation properties of redox-responsive gels based on the organometallic polymer poly(ferrocenylsilane) (PFS).

Redox-responsive organometallic networks are obtained by the incorporation of transition metals into network forming polymer chains, either as main chain constituents or included in side groups. Relatively few examples of transition-metal-based redox-active networks have appeared in the literature. For example, copolymerization of vinylferrocene with acrylamide and *N,N'*-methylenebis(acrylamide) led



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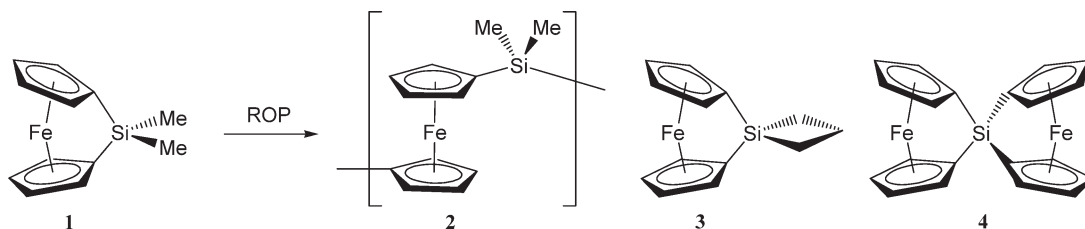
to a random copolymer gel with potential use as a glucose biosensor.^[17] A poly[(*N*-isopropylacrylamide)-*co*-vinylferrocene] gel was produced by Tatsuma et al. which displayed electrochemically and thermally controllable phase transitions.^[18] Yoshida and coworkers reported a self-oscillating redox-active gel which operated by inducing the Belousov–Zhabotinsky (BZ) reaction within a copolymer gel of *N*-isopropylacrylamide and tris(2,2'-bipyridine)ruthenium(II). The poly(NIPAM-*co*-Ru(bpy)₃) gel underwent swelling at the oxidized state and contracted in the reduced state. Due to the periodic redox changes produced by the BZ reaction within the gel, it pulsed autonomously.^[19] Other redox-responsive gels reported in the literature include a ferrocenyl surfactant system showing controlled fluid viscoelasticity,^[20] polyaniline-based gels as e.g., actuators for controlled release^[21] or catalysis,^[22] an ionically cross-linked polyphosphazene,^[23] and a poly(acrylic acid) system comprising β -cyclodextrin/ferrocenecarboxylic acid crosslinks.^[24] In the case of the latter two, crosslinks were broken and restored by redox reactions, which led to reversible swelling-contraction or sol- and gel-like behavior.

Organometallic polymers incorporating transition metals in side groups or in their main chain show great promise as constituents of redox-responsive polymer gels. Among the class of organometallic polymers, PFSs, are raising much interest due to the interesting chemical, redox, optical, thermal, and magnetic properties of these materials and due to synthetic developments which have provided access to soluble, well-defined, and well-characterized high molar mass PFS.^[25] The development of PFS, composed of alternating ferrocene and silane units in the main chain, saw a real

breakthrough in 1992 when Manners and coworkers discovered the thermal ring-opening polymerization (ROP) of strained silicon-bridged ferrocenophanes, producing high molar mass PFS.^[26] After the discovery that the strained [1]silaferrocenophanes can also be polymerized by living anionic polymerization methods, PFSs with controlled molar mass and low polydispersities became accessible.^[27] In addition, by living anionic polymerization, well-defined PFS containing block copolymers could be obtained with regular anionically polymerizable blocks such as polystyrene, polyisoprene, poly(methyl methacrylate), and many others.^[28] Other polymerization methods, such as transition metal-catalyzed ROP^[29] and photocontrolled living polymerization^[30] were subsequently developed by Manners and coworkers, broadening the range of accessible PFSs. In recent years, progress was also made in the area of water-soluble PFS polyions^[31,32] and corresponding PFS polyanionic and polycationic hydrogels.^[33] The availability of organic solvent-swallowable and water-swallowable PFS gels prompted us to summarize the progress in this field. This concise paper deals with the synthesis and properties of PFS-based organometallic gels and discusses applications, ranging from actuators to responsive polychromic photonic crystals.

Organometallic Polymer Networks

The thermal ROP of strained [1]silaferrocenophanes is a well-established route to high molar mass linear PFSs.^[26] The ability to crosslink organometallic polymers such as PFS **2** (Scheme 1) is of particular interest since crosslinking has a large influence on mechanical properties, enhances thermal stability and, in general, is known to increase ceramic yields of polymers.^[34] Moreover, crosslinking, either by permanent covalent or by reversible bonds, allows one to form organometallic gels. In chemical gels, a three-dimensional network is achieved through covalent bonds, while in physical gels the crosslinks may be formed by hydrogen bonds, crystalline regions, ionic clusters, or phase-separated microdomains.^[2d]

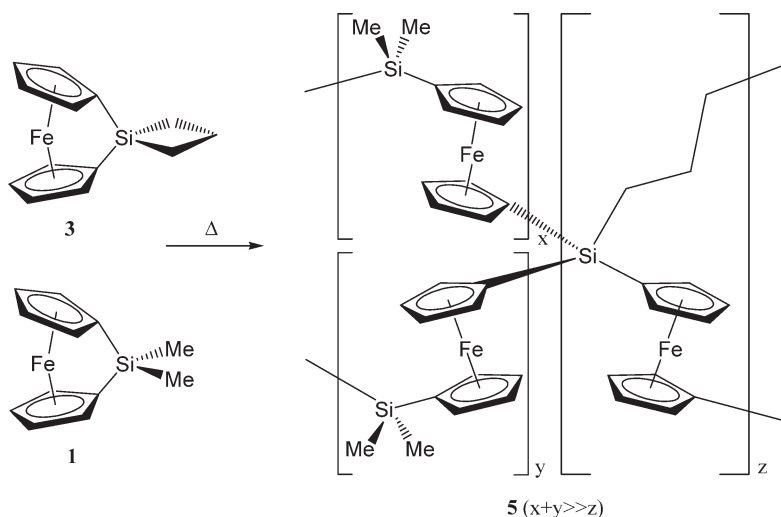


■ Scheme 1. Left: thermal ROP of strained [1]ferrocenophane **1**. Right: the spirocyclic [1]ferrocenophanes **3** and **4** can act as a crosslinker.^[35]

The first example of a covalently crosslinked PFS swellable in organic solvents was reported by Manners and coworkers in 1996.^[35] The authors found that thermal copolymerization of the chain-forming monomer **1** with desired amounts of the spirocyclic [1]ferrocenophanes **3** or **4** (Scheme 1) led to PFS networks with controlled crosslink densities (Scheme 2). The success of this universal approach was apparent from swelling experiments as will be discussed later.

Shaped Ceramics with Tunable Magnetic Properties

Poly(ferrocenylsilanes) (PFSs) have been examined as pyrolytic precursors to iron-containing ceramics due to the presence of skeletal transition metal atoms in PFS. Upon pyrolysis at 1000 °C under N₂, PFS yields a magnetic ceramic powder in low yield (30–40%) which contains ferromagnetic iron particles in a SiC–C–Si₃N₄ matrix.^[36] Thermal homopolymerization of the spirocyclic [1]ferrocenophane **3** produced a PFS network with much improved ceramic precursor characteristics due to a reduction of the amount of volatile decomposition products and due to



■ Scheme 2. Thermal copolymerization of [1]ferrocenophane **1** with the spirocyclic [1]ferrocenophane **3**, yielding PFS network **5**.^[35]

shape retention of the resulting ceramic.^[37] The spirocyclic crosslinker **3** was first polymerized at 150 °C and subsequently at 180 °C in a Pyrex polymerization tube. Analysis of the resulting crosslinked solid by ¹³C NMR and ²⁹Si CP-MAS NMR supported the assumption that thermal ROP proceeds through random ring-opening of the silacyclobutane and ferrocenophane rings and that the reactive Cp/CH₂ ends can recombine with any other Si center, leading to three possible Si microenvironments (Figure 1c). Upon heating to 600 °C under N₂, the samples heated in a tube (Figure 1a) or a pentagonal mold (Figure 1b) underwent little weight loss (90% ceramic yield) and retained their shape. The ceramic contained superparamagnetic clusters within an amorphous carbosilane matrix, which gradually (700 °C) transformed into larger clusters embedded in a

composite carbosilane–graphite matrix. Ceramics prepared below 900 °C possessed superparamagnetic iron nanoclusters. As the pyrolysis temperature increased to around 1000 °C, larger iron clusters were formed that were ferromagnetic.

Low crosslink densities already have a marked influence on the ceramic yield of PFS networks. While homopolymer **2** (Scheme 1) showed a relatively low ceramic yield of 22% at 600 °C, crosslinked networks **5a–5d** (Scheme 2) displayed an increased ceramic yield with increase in crosslink density (Table 1). The addition of only 2% crosslinking agent resulted in a 50% improvement in ceramic yield at 600 °C, by suppressing decomposition pathways which involve the loss of volatile depolymerization products.^[38] Several of these byproducts were isolated and one unusual molecular

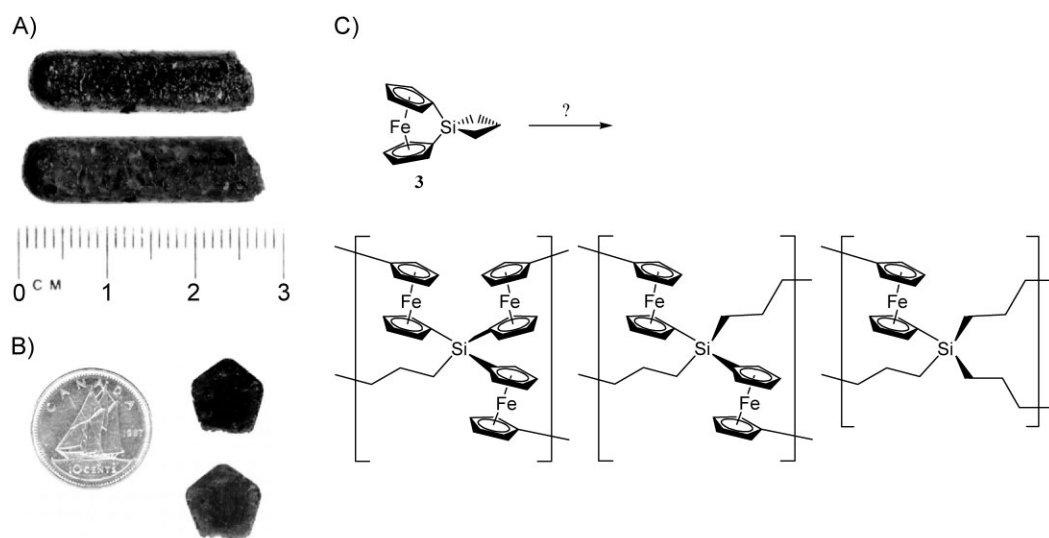


Figure 1. (A) Photographs of the bulk organometallic polymer before (bottom) and after (top) pyrolysis at 600 °C. (B) Photographs of the crosslinked spirocyclic [1]ferrocenophane **3** cast in a pentagonal Teflon mold before (bottom) and after (top) pyrolysis at 600 °C. The ceramics retain the shape of the precursor polymer and show only a small contraction after pyrolysis. Pyrolysis was not performed in a mold. (C) The three possible Si microenvironments in the crosslinked preceramic polymer network obtained by thermal polymerization of the spirocyclic crosslinker **3**. Reproduced with permission from ref.^[37] Copyright 2000, American Association for the Advancement of Science.

Table 1. Swelling experiments for samples of the thermally generated crosslinked PFSs **5a–5d**.

Polymer network ^{a)}	Mol-% of crosslinker 3	Dry mass mg	Wet mass mg ^{b)}	Mass increase %	Ceramic yield (600 °C, N ₂)
5a	2	36	130	260	31
5b	5	12	36	200	32
5c	10	43	116	170	37
5d	15	12	17	40	41

^{a)}Polymer networks **5a–5d** possess the general structure shown in Scheme 2 but have different crosslink densities due to the addition of different amounts (mol-%) of crosslinker **3**; ^{b)}the swelling solvent was tetrahydrofuran. Reproduced with permission from ref.^[35] and ref.^[38] Copyright 1996, American Chemical Society, and 2001, Springer Science + Business Media, respectively.

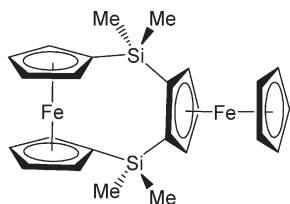


Figure 2. Depolymerization product formed during the pyrolysis of PFS homopolymer **2** under N_2 at $600^\circ C$.^[36]

depolymerization product could be identified (Figure 2).^[36] As indicated above, pyrolysis of the pure spirocyclic crosslinker **3** led to a ceramic yield of 90%.

The PFS networks **5a–5d** show an increased swelling in tetrahydrofuran as the amount of crosslinker **3** relative to the chain forming monomer **1** is decreased. This trend is consistent with a well-controlled crosslink density in these PFS networks.

Solubility Parameter for Poly(ferrocenyldimethylsilane) (PFS)

Swelling measurements on lightly crosslinked polymer networks are often used to estimate the solubility parameter of a polymer. By measuring the degree of swelling of a polymer network in a range of solvents of known solubility parameter δ , and plotting the swellability against δ , the solvent which causes maximum swelling can be identified. The δ value of this solvent is assumed to correspond to the solubility parameter of the linear homopolymer. From the swelling characteristics of a PFS network containing 4 mol-% of the spirocyclic crosslinker **3**, a solubility parameter of $\delta = 18.7 \text{ MPa}^{1/2}$ was established (Figure 3).^[38]

To gauge the influence of side group substituents at the silicon atoms on the swelling response of PFS gels, the spirocyclic [1]ferrocenophane **3** was copolymerized with a di *n*-propyl substituted [1]ferrocenophane monomer.^[38] Compared to the initially studied network chains possessing dimethyl substituents at silicon, a much stronger swelling was observed for this particular network in THF.

Polychromic Metallopolymer Gel Photonic Crystals

The response of PFS networks to solvent has been exploited to realize a colloidal photonic crystal device whose optical stop-band position, width and intensity could be reversibly solvent and redox tuned over a broad wavelength range by an anisotropic expansion of the photonic lattice.^[39] The photonic material was composed of unconnected silica microspheres embedded in a matrix of crosslinked PFS. The

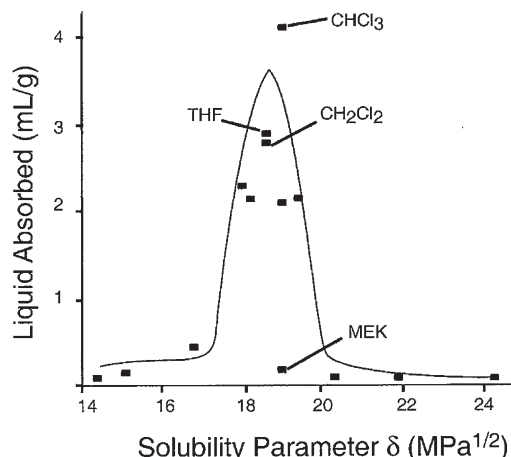
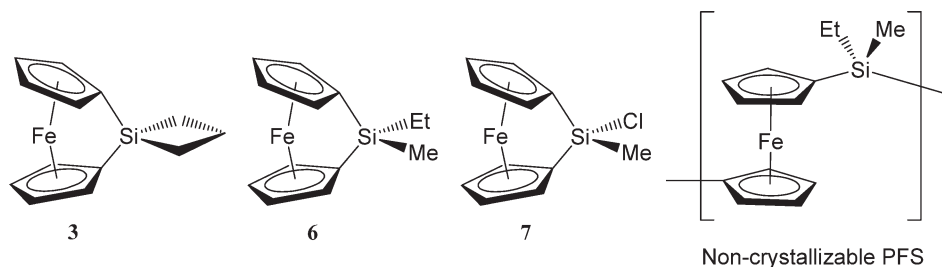


Figure 3. Relationship between the swelling ratio (mL of solvent/g of polymer) for PFS network **5** prepared using 4 mol-% of the spirocyclic crosslinker **3**, and the solubility parameter of various solvents. The region of maximum swelling occurs at $18.7 \text{ MPa}^{1/2}$. Reproduced with permission from ref.^[38] Copyright 2001, Springer Science + Business Media.

monomer employed to form the PFS network was (ethylmethyl)sila[1]ferrocenophane **6**, unsymmetrically substituted at silicon to avoid the possibility of microcrystallization within the polymer network. The spirocyclic [1]ferrocenophane **3** was used as the crosslinker (Scheme 3). Monodisperse silica microspheres were organized into planar silica colloidal crystals by the evaporative deposition method, then surface-modified with the polymerizable (chloromethyl)sila[1]ferrocenophane **7**, infiltrated with the organometallic monomers followed by thermal polymerization to yield a silica-PFS composite colloidal crystal film (Figure 4).^[39]

The fabricated composite colloidal crystal films were soaked with solvents of different solubility parameter and refractive index and, subsequently, optical properties were measured in transmission mode in a standard infrared cell mount which allowed for injection and removal of solvent. The optical characterization results were analyzed using a theoretical model based on a scalar wave approximation, allowing the authors to obtain the increase of the (111) interplanar distance $d_{(111)}$ resulting from the swelling process. To evaluate the chemomechanical response time of the composite colloidal crystal film, a kinetic experiment was conducted by collecting transmission UV–vis–NIR spectra. In order to determine when the sample had reached its fully swollen state, the maximum intensity of the first Bragg peak of the swollen sample was first noted. This wavelength was then monitored with respect to time, and carbon disulfide was injected in the sample cell. Before injecting the solvent, the absorbance was low since a background had been taken of the dry sample, and this value was constant from 0 to 7 s. Manners and coworkers



Scheme 3. Unsymmetrically substituted monomer **6** and crosslinker **3** for producing a non-crystallizable PFS network. Chlorosilane **7** is a polymerizable surface modification agent.

then saw a brief increase, which was due to scattering by the air–liquid interface created by the solvent rising in the sample cell and crossing the incident beam. Next, a sharp drop in absorbance was observed due to a decrease in refractive index contrast between the fluid content of the cell (solvent instead of air) and the various interfaces in the setup which decreased the amount of light reflected at these interfaces, resulting in more light reaching the detector. After this increase in transmitted light intensity a rapid decrease representing the swelling event was observed, after which the sample attained a steady-state transmittance value. The whole process, from initial solvent injection onto the dry polymer-silica colloidal photonic crystal sample to the completely swollen state occurred in 0.4 s. Swelling–deswelling was found to be reversible for these films (Figure 5).

In a subsequent study, Manners and coworkers exposed the PFS composite colloidal crystal film to solvent vapors to

induce swelling, controlled accurately by the solvent vapor pressure.^[40] This led to highly reproducible and repeatable changes in the optical spectra of the colloidal crystal and a full understanding of the changes occurring in the material upon solvent sorption (Figure 6).

As each repeat unit of the PFS main chain contains a redox active ferrocene unit, the redox state of the gel-forming polymer can be varied continuously by chemical and electrochemical means. Upon oxidation, the overall charge of a repeat unit changes from 0 to +1. Due to intermetallic coupling, ferrocenes in alternating positions are oxidized first, followed by oxidation of the remaining ferrocene units at a higher potential.^[41] The charge density of the PFS chain increases upon oxidation and interactions with solvents change accordingly.

Making use of the PFS redox activity, Manners and coworkers were able to fabricate full-color displays based on the electrical actuation of photonic crystals.^[42] Thin

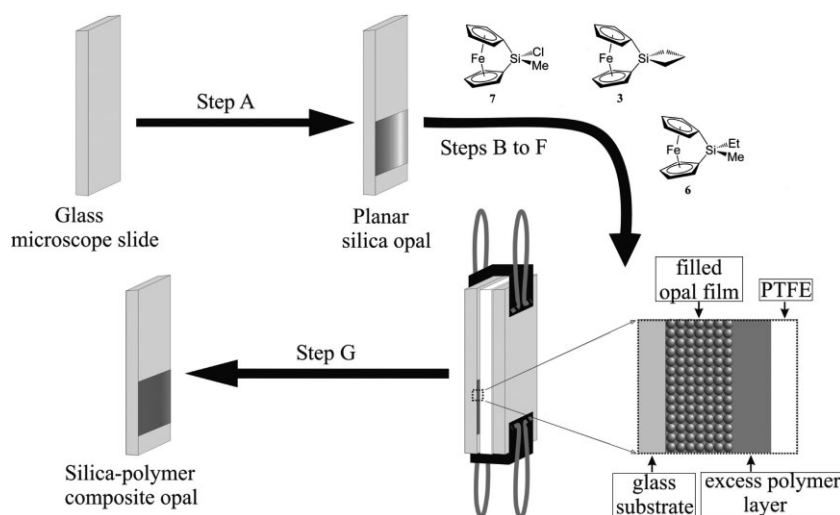


Figure 4. Schematic of steps in the fabrication of PFS composite colloidal crystal films. (A) Evaporative deposition of silica colloids. (B) 200 °C, 12 h, vacuum. (C) Treatment with capping agent **7**. (D) Infiltration of monomers **3** and **6**, removal of solvent at 300 torr. (E) Sample covered with PTFE sheet, glass slide, and bound with binder clips. (F) 190 °C, 13 h, N₂. (G) Removal of clips, PTFE, and glass cover. Reproduced with permission from ref.^[39] Copyright 2003, Springer Science + Business Media.

films of monodisperse silica spheres were deposited on indium tin oxide (ITO) coated glass plates by convective self-assembly. The voids between the silica spheres were then infiltrated by a low-molecular-weight PFS with pendant C=C containing groups, a small amount of multifunctional thiol and a radical photo-initiator. Ultraviolet irradiation led to the formation of crosslinks through the thiolene addition reaction,^[43] producing an organometallic polymer network matrix. As was the case with the previously discussed PFS networks, the degree of swelling is influenced by the type of swelling solvent and by the degree of crosslinking, which determines the ultimate range of tunability. Incorporation of the responsive colloidal composite film into an electrochemical cell in the presence of an organic solvent-based liquid electrolyte allowed reversible oxidation and reduction of the PFS network chains

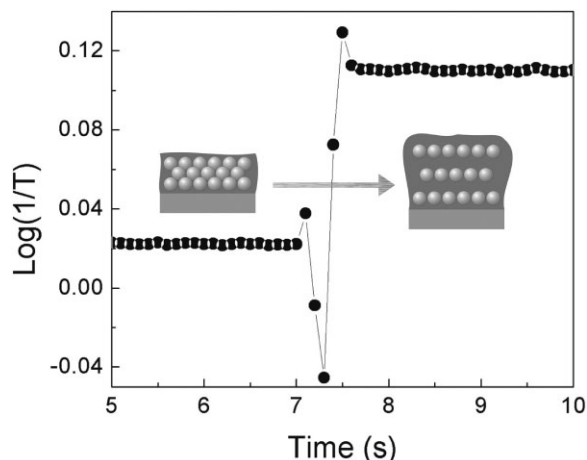


Figure 5. Kinetics plot showing the response of the silica-PFS gel composite opal upon exposure to carbon disulfide. The plot represents the absorbance at 843 nm plotted against time (0.1 s intervals) with this wavelength representing the maximum in intensity for the first stop band of the sample when swollen in carbon disulfide. The sample reaches its equilibrium swelling value within 0.2–0.4 s. Reproduced with permission from ref.^[39] Copyright 2003 Springer Science + Business Media.

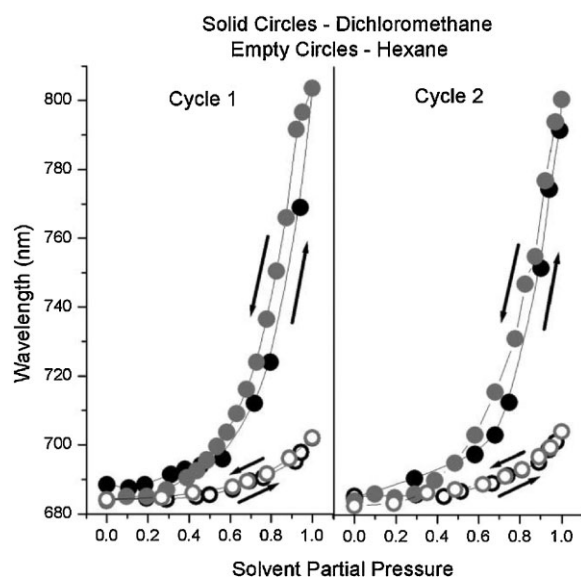


Figure 6. Experimental results showing the position of the Bragg diffraction peak of the swellable thin film colloidal crystals when exposed to two cycles of increasing and decreasing pressures of organic solvents. Data collected upon increasing the vapor pressure are shown in black, while decreasing pressure data are shown in gray. A good solvent, dichloromethane, is shown as solid circles, while a poor solvent, hexane, is shown as empty circles. The mean peak position is plotted relative to the solvent partial pressure, showing very little hysteresis in the sorption desorption behavior and reversible swelling behavior. Reproduced with permission from ref.^[40] Copyright 2005, Royal Society of Chemistry.

as well as a tunable degree of oxidation. Upon oxidation, solvated counterions migrate to the polymer chains to compensate the positive charge buildup, which causes the polymer network to swell and push apart the layers of spheres, redshifting the reflected optical diffraction peak. Upon reduction, the reverse process occurs. Owing to their continuously tunable state of oxidation, the composite colloidal films display voltage dependent continuous shifts in reflected colors. By the appropriate choice of the sphere size and crosslinker content, a single sample can be tuned to reflect all three primary colors (Figure 7). Full-color displays were fabricated based on these PFS composite colloidal films.^[42]

Redox-Responsive Poly(ferrocenylsilane) (PFS) Hydrogels for Actuation

Water soluble PFS polyions, belonging to the rare class of main chain organometallic polyelectrolytes, have been reported by us and by Manners and coworkers.^[31,32] Such materials are of interest as they can be processed in aqueous media to multilayer films, using the electrostatic self-assembly process.^[44] Following the availability of PFS polycationic species, PFS polyanions^[31d,e,32] became accessible, enabling the fabrication of all-organometallic multilayers,^[45] which are of interest e.g., due to their redox activity,^[46] as stimulus-responsive substrate-supported multilayers and as free-standing capsules with redox-responsive permeability properties.^[47] Such responsive multilayer structures may have potential for future controlled release applications.

Recently, Vancso and coworkers reported the first water-swallowable PFS networks, based on crosslinked PFS polyelectrolyte chains.^[33] The crosslinked chains possessed side groups with either permanent positive or negative charges. The aim of this work was to produce redox-responsive hydrogels that are capable of converting electrochemical stimuli into a mechanical response. A cationic PFS hydrogel was obtained in two steps. First, high molar mass poly(ferrocenyl(3-iodopropyl)methylsilane) **8** chains^[32] were crosslinked with *N,N,N',N''*-pentamethyldiethylenetriamine at room temperature to a lightly crosslinked network (Scheme 4). Subsequently, remaining iodopropyl side groups were converted into positively charged side groups by quaternization using *N,N*-dimethylethylamine, resulting in a permanently charged cationic network. Finally, iodide counterions were exchanged to chloride ions.

A polyanionic PFS hydrogel was also obtained by side group modification of poly(ferrocenyl(3-iodopropyl)methylsilane) **8**. To introduce negatively charged side groups, the carbon nucleophile α -lithio isobutyl methane-sulfonate was used.^[48] Sulfonate ester carbanions are of interest as nucleophiles, as they enable the introduction of

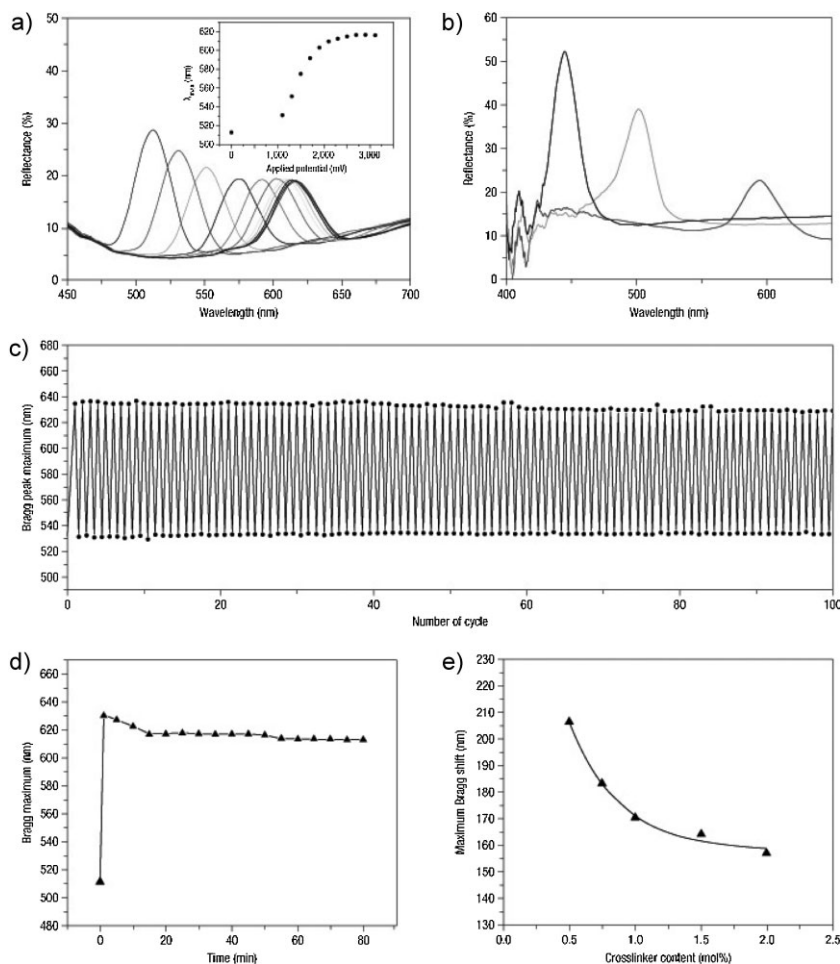


Figure 7. Electromechanochromic behavior of silica-PFS photonic crystal thin films. (a) Reflection spectra taken at increasing applied voltages. The inset shows the dependence of the peak position on the applied voltage, clearly showing a continuum of accessible colors. (b) Spectra of a sample showing reflection of all three primary colors upon incremental oxidation. (c) The Bragg peak maximum versus number of cycles for a series of 100 oxidation–reduction cycles. The voltage was cycled between 2.0 and –2.0 V, holding the sample at a particular voltage for ≈ 15 s to ensure equilibrium. (d) Electrical bistability measurement. The sample was oxidized at 2.0 V, after which the leads were disconnected and the peak position monitored as a function of time. (e) Dependence of the maximum tuning range on the crosslinker content of the composite. Reproduced with permission from ref.^[42] Copyright 2007, Nature Publishing Group.

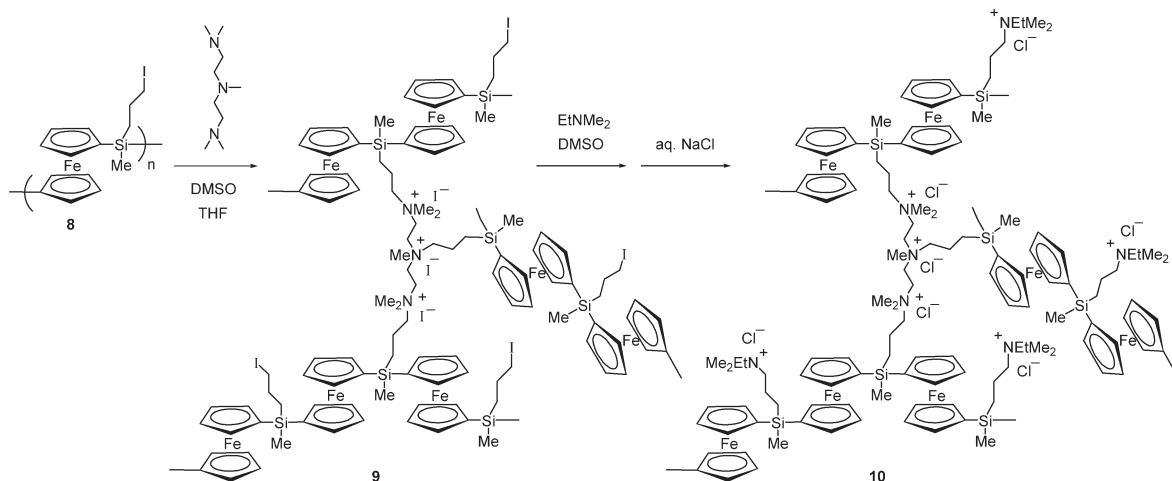
alkanesulfonate ester moieties which, after deprotection, are turned into alkanesulfonate salt functionalities. Reaction of poly(ferrocenyl(3-iodopropyl)methylsilane) **8** with one equivalent of α -lithio isobutyl methanesulfonate led to the formation of PFS network **11**, likely through intermolecular alkylation after α -deprotonation of isobutylsulfonate side groups as shown in Scheme 5. The use of an excess of α -lithio isobutyl methanesulfonate with respect to iodopropyl side groups yielded PFS with isobutylsulfonate side groups without any crosslinking.^[32] The isobutyl protecting groups were removed by heating network **11** with tetrabutylammonium iodide in THF.^[48] Exchange of

the tetrabutylammonium counterions with sodium ions in aqueous NaCl produced the polyanionic network **12**.

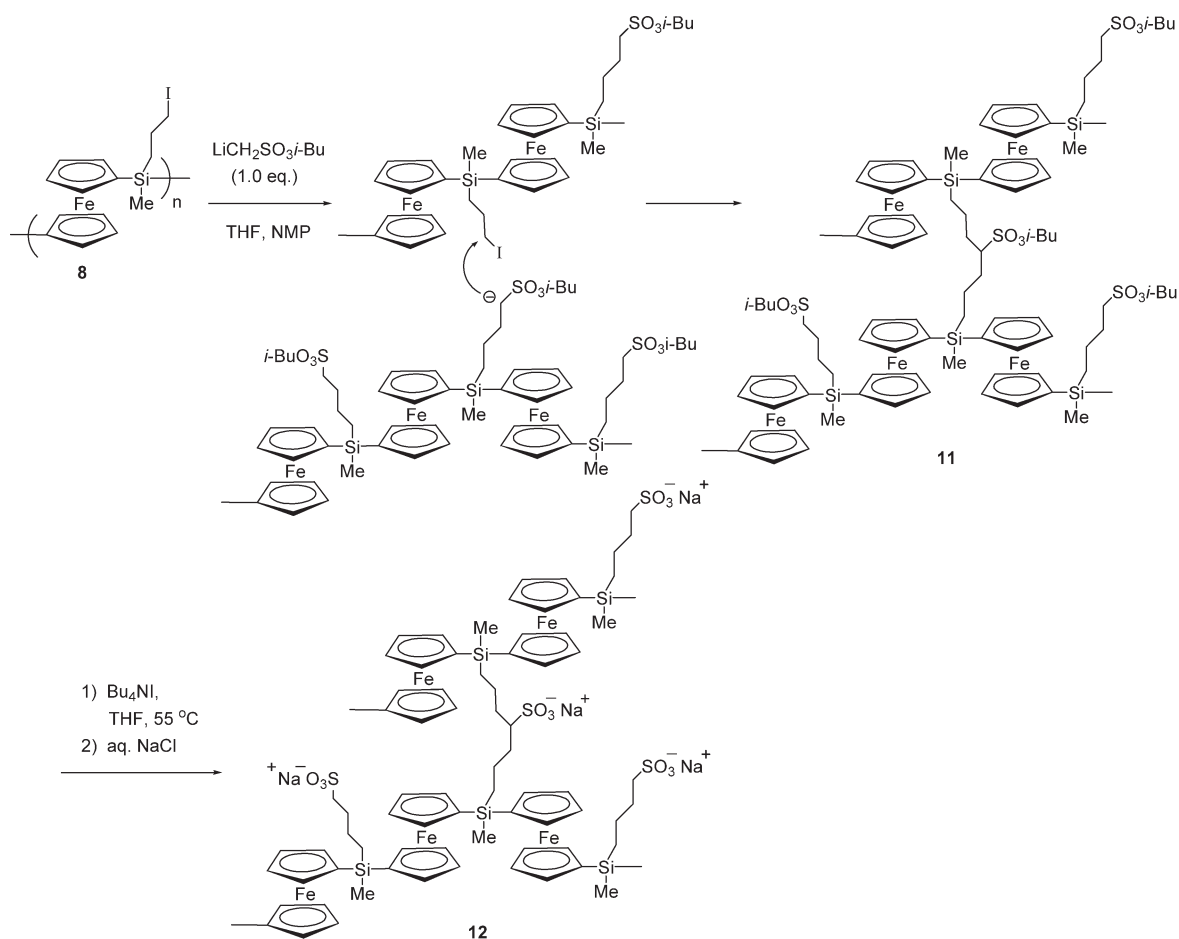
To prove that hydrogels were formed, water-uptake measurements were performed. Gel samples were subjected to several drying and hydration cycles to establish the swelling ratio^[49] (by weight) SW which was calculated as follows: $SW = (W_h - W_d)/W_d$, where W_h and W_d are the hydrated and dry sample weights, respectively (Table 2). The covalently crosslinked ionic networks showed a large water uptake and could be reversibly dried and rehydrated. Upon swelling in deionized water, the ionic PFS networks **10** and **12** became amber transparent elastic hydrogels. Swelling ratios of ± 60 and ± 120 were observed for the polycationic and polyanionic networks, respectively. The difference in swelling ratio is likely caused by a lower crosslink density of the PFS polyanion network. The obtained swelling ratios are typical of ionic networks.^[49] For instance, pH sensitive polymers incorporating *N*-acryloyl-*N'*-ethyl piperazine^[49a] or *N,N*-dimethylaminoethyl methacrylate^[49b] showed a strongly pH dependent swelling behavior, with a markedly higher water uptake under conditions when the amine groups were protonated.

The ferrocene units of the PFS chains forming the hydrogels could be reversibly oxidized and reduced by chemical and by electrochemical means. Cyclic voltammograms obtained after swelling of cationic network **10** in aqueous NaClO₄ show the two oxidation and reduction waves typical of PFSs^[41] (Figure 8).

The first oxidation and reduction waves of the hydrogels occur at relatively similar potentials. The most notable difference in the redox behavior of the hydrogels is that the polycationic hydrogel **10** shows its second oxidation wave at an ≈ 100 mV higher potential than the polyanionic hydrogel **12**, and the second reduction wave at a lower potential. Likely, full oxidation of the polycation hydrogel requires a higher potential due to electrostatic repulsion between the positively charged PFS main chains and the positively charged side groups. Upon electrochemical oxidation, the hydrogels changed color from amber to green–blue and turned back to amber upon reduction (Figure 9a–d).



Scheme 4. Synthesis of a polycationic PFS hydrogel. Poly(ferrocenyl(3-iodopropyl)methylsilane) **8** was lightly crosslinked, using a triamine, to network **9**. Unreacted iodopropyl moieties in **9** were then converted into positively charged side groups using *N,N*-dimethylethylamine (EtNMe₂). Ion exchange led to the cationic PFS hydrogel **10**.^[33]



Scheme 5. Synthesis of a polyanionic PFS hydrogel. PFS **8** was converted into a PFS featuring isobutylsulfonate side groups using α -lithio isobutyl methanesulfonate. Intermolecular alkylation resulted in network **11**. Cleavage of the isobutylsulfonate side groups and ion exchange of the resulting Bu₄N⁺ counterions to Na⁺ gave PFS hydrogel **12**.^[33]

Table 2. Poly(ferrocenylsilane) (PFS) polyion network swelling measurements in water.

Polymer ^{a)}	Dry mass	Wet mass	Swelling ratio
	mg	mg	
Polycation 10	13.3	882	65.3
Polyanion 12	10.1	1260	123.7

^{a)} Polyion network structures are displayed in Scheme 4 and 5. Reproduced with permission from ref.^[33] Copyright 2009, American Chemical Society.

A mechanical testing device (Figure 10, left), developed at the University of Catania, Italy was employed to study the responses of the polyanion hydrogel upon electrochemical oxidation and reduction. The device was equipped with a potentiostat which controlled the degree of charging of the hydrogel, and a load cell to gauge any responses of the hydrogel upon changing its oxidation state. A sample of PFS polyanion hydrogel (diameter 5.2 mm, height 4 mm) was first oxidized and subsequently reduced back to its neutral state. Upon oxidation, electrostatic attractions between the generated positive charges in the PFS main chains and

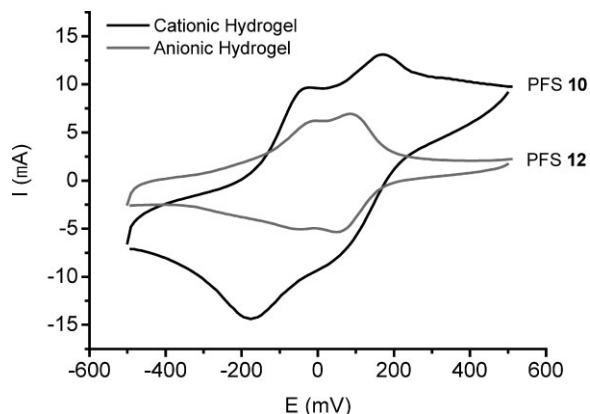


Figure 8. Cyclic voltammograms of the polycationic PFS hydrogel **10** and the polyanionic hydrogel **12**, swollen in 0.1 M NaClO₄. Scan rate: 50 mV · s⁻¹.

the negatively charged sulfonate side groups caused the hydrogel to collapse. Subsequent reduction removed this internal charge compensation and allowed the PFS chains to regain their polyanionic nature. The hydrogel reswelled and in this process it exerted a pressure of 50 Pa (Figure 10, right). Work in progress includes a detailed study of this collapse/reswelling behavior and of the mechanical properties of the polyanionic hydrogel as a function of its redox state.

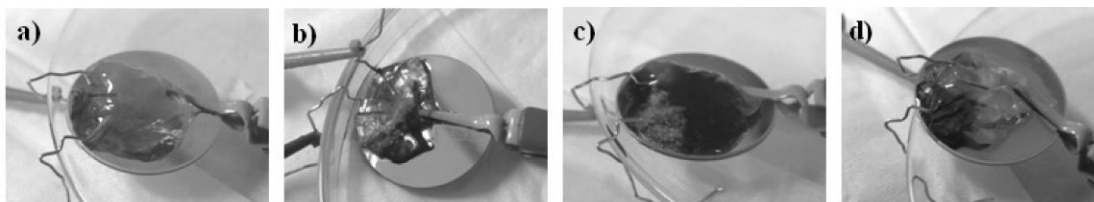


Figure 9. Electrochemical oxidation and reduction of polyanionic hydrogel **12**, swollen in aqueous NaClO₄ and supported on a gold electrode. (a) Neutral amber colored PFS hydrogel; (b) oxidation starts, accompanied by a color change from amber to blue-green; (c) Fully oxidized PFS hydrogel; (d) Electrochemical reduction of the PFS hydrogel has almost completed, the color changed back from blue-green to amber.

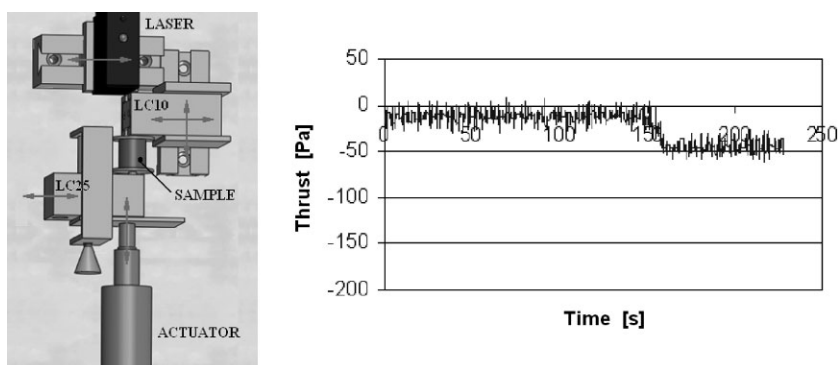


Figure 10. Left: detail of the testing machine designed for the mechanical characterization of hydrogel responses. The degrees of freedom of each component are indicated by the arrows. Right: mechanical response upon reduction of oxidized PFS polyanionic hydrogel **12**. A pressure of 50 Pa was exerted by the hydrogel sample (diameter 5.2 mm, height 4 mm) upon electrochemical reduction.

Conclusion

In summary, organometallic gels based on lightly crosslinked PFS networks form a fascinating new class of stimuli-responsive materials which allow one to make use of classical stimuli such as tuning solvent type and solvent vapor pressure to induce a response, but also provide the opportunity to address the network chains by redox chemistry. Using electrochemical stimuli, the PFS chains in the gel can be oxidized and reduced reversibly and in a continuous fashion. This enables one to accurately control polymer–solvent interactions and thereby the swelling or deswelling of the gels, which serves as a method for actuation, as was illustrated by the electrochemical actuation of colloidal photonic crystals leading to full-color displays. In a second example of redox-mediated actuation, hydrogels of cationic and anionic PFS strong polyelectrolytes were obtained by covalent crosslinking approaches.^[33] The networks showed a strong swelling in water and could be reversibly hydrated and dehydrated. The extent of charging could be controlled by the redox voltage. A striking feature in the response characteristics of the PFS hydrogels is that complete oxidation and reduction only require applied voltages of less than 0.5 V. In case of the polyanionic hydrogel, oxidation–reduction cycles led to a reversible collapse and reswelling of the network. During reswelling, a measurable pressure was exerted by the hydrogel, which implies that such systems could be used in artificial muscle applications.

Future development of the PFS polyion hydrogels will involve the further exploration of covalent crosslinking methodologies such as the azide-alkyne Huisgen cycloaddition reaction (click chemistry) or thiolene chemistry. However, PFS networks that are based on physical, reversible interactions between the PFS chains should also be considered, as such materials potentially could combine stimulus-responsive and self-healing characteristics.

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