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Living Photolytic Ring-Opening Polymerization of Amino-Functionalized [1]Ferrocenophanes: Synthesis and Layer-by-Layer Self-Assembly of Well-Defined Water-Soluble Polyferrocenylsilane Polyelectrolytes

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Abstract: Facile synthetic routes have been developed that provide access to cationic and anionic water-soluble polyferrocenylsilane (PFS) polyelectrolytes with controlled molecular weight and narrow polydispersity. Living photolytic ring-opening polymerization of amino-functionalized [1]ferrocenophane (fc) monomers $[fcSiMe\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\}]$ (**3**), $[fcSi\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\}_2]$ (**10**), $[fcSiMe(C{\equiv}CCH_2NMe_2)]$ (**14**), and $[fcSiMe(p\text{-}C_6H_4CH_2NMe_2)]$ (**20**) yielded the corresponding polyferrocenylsilanes $[(fcSiMe\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\})_n]$(**5**), $[(fcSi\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\}_2)_n]$ (**11**), $[\{fcSiMe(C{\equiv}CCH_2NMe_2)\}_n]$ (**15**), and $[\{fcSiMe(p\text{-}C_6H_4CH_2NMe_2)\}_n]$ (**21**) with controlled architectures. Further derivatization of **5**, **15**, and **21** generated water-soluble polyelectrolytes $[(fcSiMe\{C{\equiv}CCH_2N(CH_2CH_2CH_2SO_3Na)_2\})_n]$ (**6**), $[\{fcSiMe(C{\equiv}CCH_2NMe_3OSO_3Me)\}_n]$ (**7**), and $[\{fcSiMe(p\text{-}C_6H_4CH_2NMe_3OSO_3Me)\}_n]$ (**22**), respectively. The polyelectrolytes were readily soluble in water and NaCl aqueous solutions, with **6** and **22** exhibiting long-term stability in aqueous media. The PFS materials **6** and **22**, have been utilized in the layer-by-layer (LbL) self-assembly of electrostatic superlattices. Our preliminary studies have indicated that films made from controlled low molecular-weight PFSs possess a considerably thinner bilayer thickness and higher refractive index than those made from PFSs that have an uncontrolled high molecular-weight. These results suggest that the structure and optical properties of LbL ultrathin films can be tuned by varying polyelectrolyte chain length. The water-soluble low molecular weight PFSs are also useful materials for a range of applications including LbL self-assembly in highly confined spaces.

Keywords: ferrocene · metallopolymers · photolysis · polyelectrolytes · self-assembly

Introduction

Water-soluble polyelectrolytes are a class of polymers that are of significant importance for industrial applications and for the development of advanced materials.[1] These macromolecules have attracted much recent attention as building blocks in the layer-by-layer (LbL) self-assembly of electrostatic superlattices, in which oppositely charged monolayers are adsorbed sequentially from aqueous solutions onto a substrate surface. The resulting multilayer thin films possess a layer thickness on the nanometer scale and have been utilized extensively in areas such as surface modification and patterning, the manufacturing of thin film devices, and controlled drug release.[2,3] Moreover, recent advances in polymer synthesis have provided access to selected organic polyelectrolytes that have controlled molecular weight and narrow polymer size distribution. This has greatly facilitated the development of new classes of polymeric materials such as amphiphilic block copolymers, which possess hydrophilic and hydrophobic blocks of controlled size and have been used to prepare self-assembled micelles and vesicles that are promising materials for various applications ranging from controlled drug delivery to biomimetic membrane development.[4] Despite extensive studies of organic polyelectrolytes,

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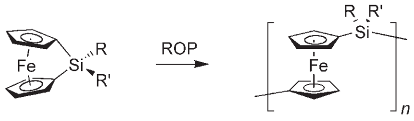
however, reports on inorganic polyelectrolytes are rare, in particular those with well-controlled architectures. This is especially the case for transition metal-containing polymers, which would be expected to bring many attractive features, such as conductive, optical, redox, and catalytic properties to diverse advanced materials development and applications.[5–7]

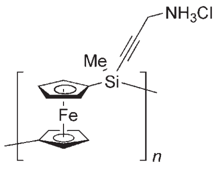
Polyferrocenylsilanes (PFSs) **2** are a class of high molecular weight metal-containing macromolecules that were developed in the early 1990s through ring-opening polymerization (ROP) of strained sila[1]ferrocenophanes **1** (Scheme 1).[5,8] These polymers possess a range of interesting properties including reversible redox activity, semiconductivity upon oxidation, and tunable magnetic properties upon pyrolysis.[5,9–15] In addition, PFS block copolymers obtained through anionic ROP have provided access to highly ordered phase-separated domains in the solid state and self-assembled micelles in solution.[16,17] Many other areas that have potential PFS applications include microsphere technology,[18] radiation protective coatings,[19] photonic band gap materials,[20,21] variable refractive index sensing materials[22] and etch resists.[23]

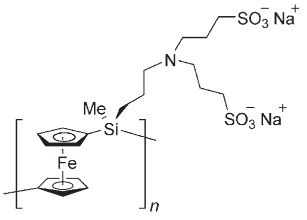


1 **2**

Scheme 1.

The recent development of water-soluble PFSs has provided several of the first metallopolyelectrolytes that possess transition metals in the main chain (shown here).[6,24–27]





These polyelectrolytes have been used as building blocks in the LbL assembly of organometallic–organic and all organometallic electrostatic superlattices, which have found applications in materials science, such as redox-tunable capsules and the tuning of optical properties of photonic crystals.[27–30] Despite the recent advancement in the area of water-soluble metallomacromolecules, polyelectrolytes which possess transition metals in the main chain have yet to be obtained with controlled molecular weight and narrow molecular weight distribution.[5,6] It is anticipated that the development of metallopolyelectrolytes with controlled architectures will not only facilitate the fundamental studies of these macromolecules and their multilayer films, but also help expand the scope of their applications in materials science to include controlled LbL assembly and the development of amphiphilic metallo block copolymers and materials.

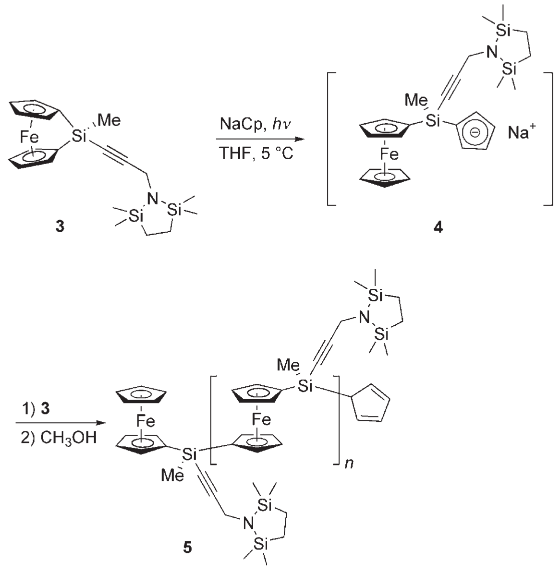
With these objectives in mind, we explored the synthesis of well-defined PFS polyelectrolytes through anionic ROP of strained ferrocenophanes, as molecular weight control was difficult to achieve in thermal and transition metal-catalyzed ROP.[24,26,27] However, the anionic route was found to be unsatisfactory due to side reactions of the functional groups in the monomers with the anionic *n*-butyllithium initiator and propagating chain ends. Recently, a new living polymerization method, photolytic ring-opening polymerization (PROP), has been developed in the synthesis of alkyl- and aryl-PFSs with good molecular weight control.[31–33] One of the attractive features of this method is the mild reaction conditions, which we anticipated would be more tolerant toward the functional groups that are unstable in anionic polymerizations. In this paper we report full details of photolytic polymerization of functionalized ferrocenophane monomers, and the first synthesis of water-soluble cationic and anionic PFS polyelectrolytes, which possess well-controlled architectures with desired molecular weight and narrow polydispersity. Our work on the LbL assembly of these polyelectrolytes and preliminary study on the effect of polymer molecular weight on the structure and property of the resulting multilayer films is also discussed.

Results and Discussion

To develop a general synthetic pathway that could provide access to PFS polyelectrolytes with well-controlled architectures, we examined ROP of a range of [1]ferrocenophanes with various amino-functionalized substituents under photolytic polymerization conditions. Further derivatization of the resulting polymers was anticipated to afford the desired macromolecules that have cationic and anionic water-soluble groups along the polymer chain.

PROP of the silicon-bridged [1]ferrocenophane 3—synthesis and characterization of protected aminopropynyl PFS 5: The silicon-bridged [1]ferrocenophane **3**, which has a protected amino group, was used in the photolytic ring-opening polymerization as it had been demonstrated in our previous work that the silyl protective group can be removed under mild conditions.[26] It was anticipated that the resulting amino PFS would serve as a precursor to both cationic and anionic water-soluble PFSs.

PROP of [1]ferrocenophane **3** was carried out in the presence of 0.1 equivalents of anionic initiator sodium cyclopentadienylide in THF and exposure to UV/Vis irradiation at 5 °C (Scheme 2). After 2 hours of stirring, the color of the reaction solution turned from red to orange, indicating the successful ring opening of the monomer. Precipitation of the reaction mixture into degassed methanol afforded PFS **5** as



Scheme 2.

an orange-yellow gummy material. Gel permeation chromatography (GPC) analysis of the product showed that the material possessed a desired low molecular weight and narrow polydispersity. In the numerous polymerization experiments that we carried out, PFS **5** was obtained with a PDI generally in the range of 1.10–1.20 and a molecular weight ranging from $M_n = 3.9 \times 10^3$ to 6.3×10^3, which corresponds to approximately 9–15 monomeric units. End-group analysis of the polymer by ^{1}H NMR spectroscopy indicated that the number-average degree of polymerization (DP_n) was usually in the range of 8–14.

By varying the monomer/initiator ratio, the protected aminopropynyl polyferrocenylsilane can be obtained with controlled architectures at higher molecular weight. Thus, PFS **5** was prepared with 20, 50, 100 and 200 repeat units, which corresponds to molecular weights in the range of $M_n \approx 1.1 \times 10^4$–$7.1 \times 10^4$. All polymers were characterized by using ^{1}H NMR spectroscopy and GPC, and the results are summarized in Table 1. For a monomer/initiator ratio of up to $\approx$100, polymer **5** can be obtained with relatively low polydispersity. In addition, the molecular weights acquired by using GPC were in good agreement with those obtained from NMR end-group analysis and the theoretical calculations based on the monomer/initiator ratio. The polymer molecular weight from theoretical calculation and experimental data is plotted against the monomer/initiator ratio in Figure 1, which shows that excellent molecular-weight control can be achieved for polymers that have a M_n of up to 4.4×10^4 through PROP. At higher monomer/initiator ratios of $\approx$200, however, polymer **5** was obtained with large polydispersity and a molecular weight much lower than the calculated theoretical value (Table 1, entry e). Moreover, bimodal molecular weight distribution has been observed in some instances. It is unclear as to what might have caused such deviation in the polymer molecular weight at the high monomer/initiator ratio, but the reaction of impurities with propagating sites provides a possible explanation.

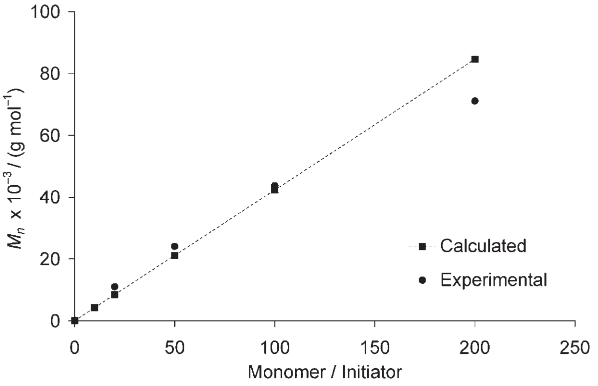


Figure 1. Variation of molecular weight of polymer **5** with monomer/initiator ratio, [M]/[I], as calculated (■) and obtained by GPC (●).

Polyferrocenylsilane **5** was characterized by using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and its structure was confirmed by data comparison with high molecular-weight polymer previously synthesized through transition metal-catalyzed ring-opening polymerization.[26] Since we were able to obtain **5** with desired short chain lengths, protons at the chain ends can be clearly observed in the ^{1}H NMR spectrum. For example, in the case of PFS **5** ($DP_n \approx 10$), the η^5-C_5H_5 protons at the ferrocenyl end of the polymer chain exhibited a chemical shift at 4.21 ppm, slightly upfield from the rest of the ferrocenyl protons in the main chain (4.23–4.72 ppm). A similar trend was observed for the methylene protons adjacent to the acetylene moiety on the chain ends at 3.66 and 3.64 ppm, upfield from the principal peak of those in the main chain at 3.68 ppm. In addition, the methyl protons in the cyclic disilyl protective group appeared as a slightly broadened single peak at 0.27 ppm, and a small signal at 0.25 ppm corresponds to those at the Cp end of the chain. The carbons of the capping Cp (η^5-C_5H_5) on the ferrocenyl end of the polymer chain were also clearly observed at

Table 1. Summary of data for polymer **5** synthesized by PROP.

Sample	[M]/[I][a]	$DP_{n,NMR}$[b]	$M_{n,calc}$[c]	$M_{n,GPC}$	PDI[d]	t [h]	Yield of PFS **5** [%]	Yield of (−)PFS **6** [%]
a	10	8	4230	3900	1.14	2.5	70	91
b	20	25	8460	11000	1.24	4	48	83
c	50	55	21150	24100	1.32	4	59	85
d	100	115	42300	43700	1.08[e]	5	65	80
e	200	–	84600	71100	2.13[e]	6	90	88

[a] [M]/[I] denotes monomer:initiator ratio. [b] Values determined by ^{1}H NMR integration of Cp polymer protons relative to the Cp end-group protons. [c] Cp end groups are not included. [d] Given by M_w/M_n from GPC analysis. [e] Polymer was isolated by solvent removal under vacuum without being precipitated in methanol.

69.5 ppm in the ^{13}C NMR spectrum, upfield from the ferrocenyl Cp ligands in the polymer main chain ($\delta = 69.8$–74.8 ppm). Notably, the η^5-C_5H_5 protons at the ferrocenyl end of the polymer chain can be detected in the ^{1}H NMR spectra of PFS **5** at a molecular weight of up to $M_n = 4.4 \times 10^4$. This allows the estimation of the degree of polymerization ($DP_{n,NMR}$) for polymers with repeat units of up to 100 by using end-group analysis through integration of the Cp protons in the end group and the polymer main chain.

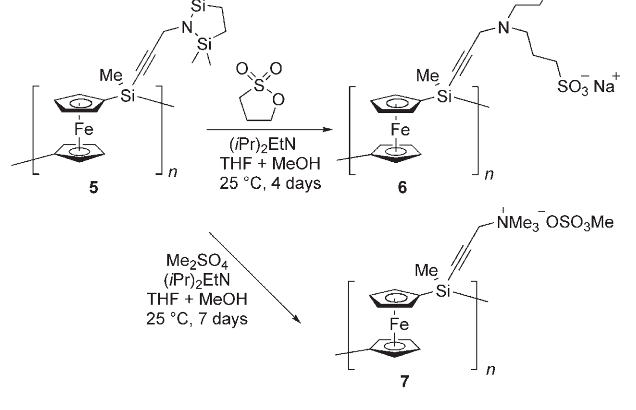
The proposed reaction pathway in PROP involves the activation of the Fe−(η^5-C_5H_4) bond in the strained sila [1]ferrocenophane [(η^5-C_5H_4)Fe(η^5-C_5H_4)SiMe{C≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$}] (**3**) with exposure to UV/Vis irradiation.[33] In the presence of a cyclopentadienylide initiator such as Na[C_5H_5], the ring-strain in the monomer is relieved through the photoactivated replacement of a η^5-C_5H_4 moiety by the [C_5H_5]$^-$ anion in the initiator (Scheme 2).[31–33] The anionic end group in the newly generated intermediate species Na$^+$ [(η^5-C_5H_5)Fe(η^5-C_5H_4)SiMe{C≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$}(C_5H_4)]$^-$ (**4**) undergoes further propagation with other activated ferrocenophane monomers. Finally, termination of the polymerization by methanol quenching affords PFS **5** as the desired product.

Synthesis and characterization of anionic PFS 6 and cationic PFS 7 with controlled architectures: The synthesis of anionic PFS **6** was achieved under mild conditions in a one-pot procedure in which the protected aminopropynyl PFS **5** was used in a reaction with 1,3-propane sultone in the presence of an excess amount of diisopropylethylamine in a mixture of THF and methanol solvents (4:1 v/v) (Scheme 3).[26] The polyelectrolyte **6** thus obtained was highly soluble and exhibited long-term stability in water and aqueous NaCl solutions. The structure of PFS **6** was confirmed by comparing its ^{1}H, ^{13}C, and ^{29}Si NMR data with that of the high molecular-weight analogue previously reported in the literature.[26]

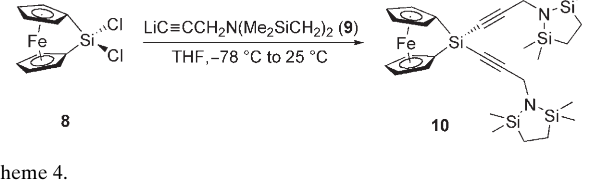
The conversion of PFS **5** to cationic polyelectrolyte **7** was carried out in a mixture of THF and methanol solvents (4:1, v/v) in the presence of an excess amount of dimethyl sulfate and diisopropylethylamine (Scheme 3). Therefore, removal of the silyl protective groups in PFS **5** followed by quaternization of the amino moieties afforded polyelectrolyte **7**, which was soluble in water and methanol. Although also soluble in aqueous 0.1 M NaCl solutions, the polyelectrolyte remained stable only for a short period of time and precipitated after two weeks.

The cationic PFS **7** was characterized by using ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum obtained in D_2O indicated the successful removal of the protective groups in polymer **5** by the absence of the methyl and methylene protons in the cyclic disilyl moiety ($\delta = 0.27$ and 0.79 ppm, respectively). In addition, a single peak was observed at $\delta = 3.22$ ppm which corresponds to the methyl protons in the quaternary ammonium group. Furthermore, the resonance of the methylene protons adjacent to the nitrogen atom was shifted significantly downfield from $\delta = 3.68$ ppm in protected aminopropynyl PFS **5** to $\delta = 4.00$ ppm in the cationic polyelectrolyte **7**, merging with the signals of the ferrocenyl protons in the region of $\delta = 4.00$–4.73 ppm. This is consistent with our previous observation that the methylene protons adjacent to an amino group became less shielded upon quaternization of the amino moiety.[25,26] The ^{13}C NMR spectrum of **7** also supported the assigned structure. For example, the resonances of the methyl and methylene carbons in the protective groups of **5** were absent from the spectrum of **7**. And the methylene carbon adjacent to the nitrogen atom exhibited a chemical shift of $\delta = 56.8$ ppm, a significant downfield shift from its resonance at $\delta = 32.4$ ppm in the protected aminopropynyl PFS **5**. The ^{1}H and ^{13}C NMR results confirmed that >96% of the amino groups had been successfully quaternized.

PROP of the silicon-bridged [1]ferrocenophane 10—synthesis and characterization of protected aminopropynyl PFS 11: After the successful polymerization of the protected aminopropynyl monomer **3**, we next examined ferrocenophane **10** under the same photolytic ROP conditions with the aim to obtain a controlled polyelectrolyte architecture which possesses two water-soluble ammonium groups in each repeat unit. Monomer **10** was therefore synthesized from dichloro sila [1]ferrocenophane **8**[34] in a nucleophilic substitution reaction with LiC≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$ (**9**), which was generated in situ from protected propargylamine HC≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$[26] and n-butyllithium at −78 °C (Scheme 4). Recrystallization of the crude product in hexanes at −35 °C afforded **10** as a red solid. Characterization by using ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy as well as mass spectroscopy



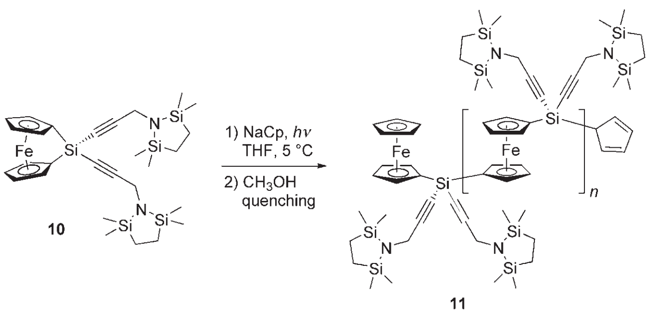
Scheme 3.



Scheme 4.

afforded data that were consistent with the assigned structure.

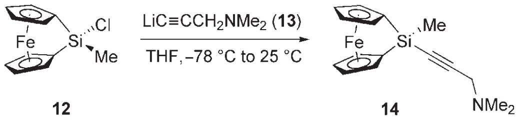
Polymerization of monomer **10** proceeded smoothly under the aforementioned PROP conditions in the presence of 0.1 equivalents of NaCp (Scheme 5). PFS **11** was obtained as an orange gummy material with a molecular weight of $M_n = 4.9 \times 10^3$ and a PDI of 1.13 by using GPC analysis, corresponding to ≈8 monomeric units. The polymer was characterized by using ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy and the data were found to be in accordance with the assigned structure. Two signals were detected in the ^{29}Si NMR spectrum at $\delta = 14.9$ and -45.8 ppm, corresponding to the silicon environments in the protective group and the main chain of the polymer, respectively. In the ^{13}C NMR spectrum of **11**, the Cp *ipso*-carbon was detected at $\delta = 67.7$ ppm, a significant downfield shift from that in monomer **10** at $\delta = 31.9$ ppm. This was in agreement with our previous observations that the release of ring-strain in ferrocenophane monomers through ring-opening polymerization leads to a downfield shift of the *ipso*-carbon signals.[26,34] As shown in the ^{13}C NMR spectrum of PFS **5**, the carbons of the capping cyclopentadienyl moiety (η^5-C_5H_5) on the ferrocenyl end of polymer **11** were clearly observed at $\delta = 69.9$ ppm. In addition, two resonances characteristic of the acetylenic carbons from the aminopropynyl substituents were detected at $\delta = 82.8$ and 109.9 ppm. The ^{1}H NMR spectra was also consistent with the assigned structure.



Scheme 5.

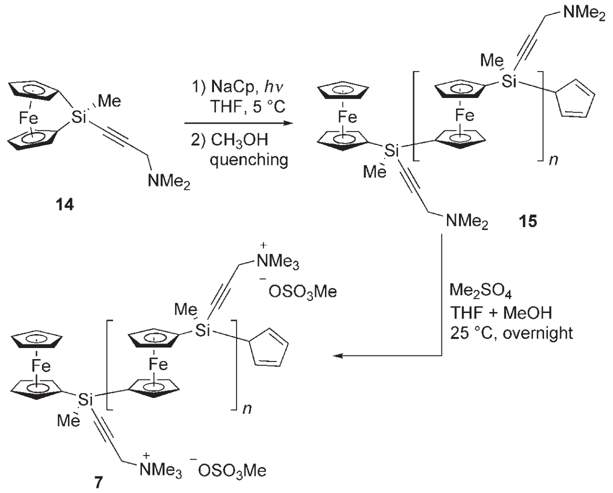
Deprotection and quaternization of the amino groups in **11** was carried out in a one-pot procedure as described in the synthesis of PFS **7**. However, the polymer formed cross-linked material after several hours of stirring, which could not be re-dissolved in commonly used solvents.

Synthesis and PROP of silicon-bridged dimethylaminopropynyl[1]ferrocenophane 14—development of dimethylaminopropynyl PFS 15 and cationic PFS 7: The silicon-bridged [1]ferrocenophane **14** presents an interesting monomer for PROP studies as it possesses an unprotected tertiary amine functionality, which may potentially interfere with the polymerization process. Meanwhile, in comparison to the protected amino groups in PFS **5**, quaternization of the tertiary amino group was expected to be more straight forward as it does not require an extra deprotection step. This makes monomer **14** an attractive precursor for the potentially facile access to cationic PFS **7**. Thus, monomer **14** was prepared from the substitutionally labile sila[1]ferrocenophane **12**[34] in a nucleophilic reaction with 3-dimethylamino-1-propynyl lithium (**13**) (Scheme 6). Recrystallization in hexanes at −35 °C followed by vacuum sublimation (0.05 mmHg) of the crude product at 70–75 °C afforded **14** as a dark red crystalline solid in moderate yield (63 %). Monomer **14** was characterized by using ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy and the data collected were in agreement with the assigned structure.



Scheme 6.

In the presence of 0.1 equivalents of the anionic initiator sodium cyclopentadienylide, PROP of monomer **14** in THF proceeded smoothly with exposure to UV/Vis irradiation at 5 °C for 2.5 h (Scheme 7). Quenching of the reaction with degassed ethanol, followed by precipitation of the crude product into methanol, afforded dimethylaminopropynyl PFS **15** as an orange gummy material in good yield (≈80 %). The polymer was soluble in common organic solvents such as benzene, THF and dichloromethane. GPC analysis showed that it possessed a molecular weight of $M_n = 3.4 \times 10^3$ and a narrow PDI of 1.08, which corresponds to ≈11 repeat units in each chain.

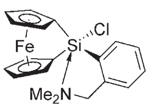


Scheme 7.

Polymer **15** was characterized by using ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy. The ^{29}Si NMR signal was detected at $\delta = -24.7$ ppm, analogous to that observed in the protected aminopropynyl PFS **5** ($\delta = -24.8$ ppm) and shifted downfield from the bridging silicon atom in monomer **14** ($\delta = -28.7$ ppm). In the ^{13}C NMR spectrum of polymer **15**, the resonance of the *ipso* carbons ($\delta = 69.9$ ppm) was shifted significantly downfield from that in monomer **14** ($\delta = 31.0$ ppm), as a result of the release of ring strain in the ferrocenophane monomer.[26,34] As shown in the ^{13}C NMR spectra of PFSs **5** and **11**, the carbons of the capping cyclopentadienyl moiety (η^5-C_5H_5) at the ferrocenyl end of polymer **15** were clearly observed at $\delta = 69.5$ ppm. The ^1H NMR spectroscopy data of **15** was also consistent with the assigned structure.

The dimethylamino groups in polyferrocenylsilane **15** were converted to ammonium moieties in a reaction with dimethyl sulfate in a mixed solvent of THF and methanol (4:1, v/v) (Scheme 7). As the reaction proceeded, some of the cationic polymer formed during the quaternization precipitated. To ensure all the amino groups were quaternized, methanol was added to dissolve the precipitates and the reaction mixture was allowed to stir overnight. Purification of the crude product by precipitation in THF afforded the cationic polymer **7** as an orange powder, which was readily soluble in methanol, water, and NaCl solutions. However, as with the cationic polyelectrolyte obtained from the protected PFS **5**, polymer **7** was unstable in 0.1 M NaCl solutions and precipitated after two weeks. The precipitate was not soluble in common organic solvents and water, even at elevated temperatures.

Synthesis and characterization of *p*-(dimethylaminomethyl)phenyl sila[1]ferrocenophane 20: A monomer that was of significant interest to us was *o*-(dimethylaminomethyl)phenyl sila[1]ferrocenophane **16** [35] as it had been previously demonstrated that the thermal ROP of **16** affords a (dimethylaminomethyl)phenyl PFS, which can be readily converted to the cationic phenyl polyferrocenylsilane **17**.[24] This polyelectrolyte is stable in NaCl solutions and has been used extensively in the LbL assembly of PFS multilayers.[28,30] However, although ferrocenophane **16** readily undergoes thermal polymerization, ring opening of this monomer under photolytic conditions was sluggish. A significant amount of monomer **16** was detected in the reaction mixture even after 5–7 hours of UV/Vis irradiation.



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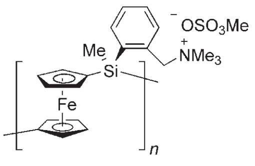

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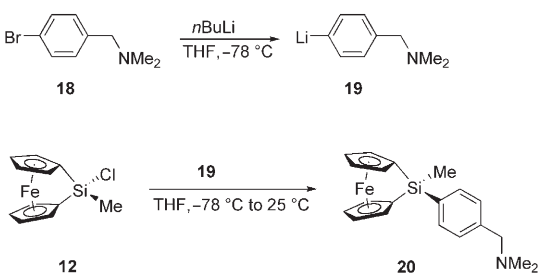
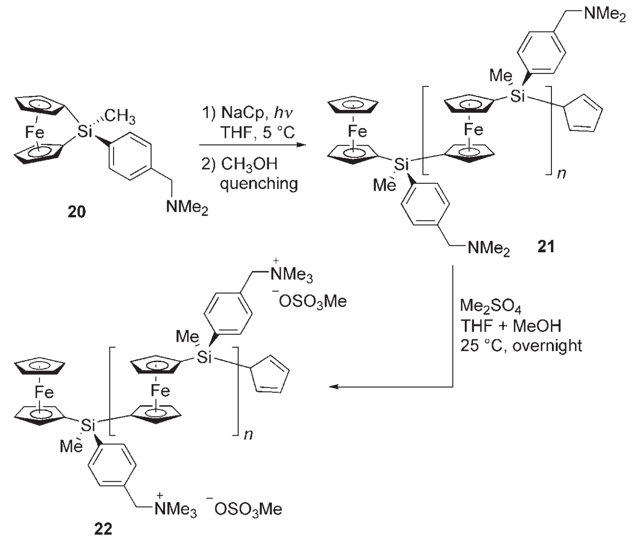
The sluggishness of the polymerization was probably a result of the relatively close proximity of the dimethylamino group and the iron center in the monomer, which may favor intramolecular chelation between the two moieties and, therefore, hinder effective ring opening of the monomer. This problem could be circumvented by using a monomer in which the dimethylamino group is further removed from the iron center. Therefore, *p*-(dimethylaminomethyl)phenyl sila[1]ferrocenophane **20** was synthesized as illustrated in Scheme 8. Halogen-metal exchange between 4-bromobenzyldimethylamine **18**[36] and *n*-butyllithium yielded the phenyl lithium species **19**,[37] which was subsequently used in the nucleophilic substitution reaction with chloro methyl[1]-ferrocenophane **12** to afford monomer **20** as a dark red crystalline solid.



Scheme 8.

Ferrocenophane **20** was characterized by using ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and the data were consistent with the assigned structure. Most notable in the ^1H NMR spectrum were the phenyl proton resonances which were observed as two doublets at $\delta = 7.48$ and 7.96 ppm. This indicated that the lithium–bromide exchange took place exclusively at the *para* position of the phenyl ring, which was preserved in the subsequent reaction with the chloro ferrocenophane **12**. The detection of four carbon signals in the phenyl region of the ^{13}C spectrum further confirmed that the dimethylaminomethyl group was *para* to the silyl moiety on the phenyl ring.

PROP of the silicon-bridged [1]ferrocenophane 20—synthesis and characterization of PFS 21: Under exposure to UV/Vis irradiation, the photolytic polymerization of monomer **20** proceeded smoothly in the presence of 0.1 equivalents of NaCp (Scheme 9). After 3 hours of stirring, the color of the reaction solution changed from dark red to orange, indicating that most of the monomer had been consumed. Precipitation of the crude product in methanol gave polymer **21** as an orange gummy material, which was soluble in common organic solvents such as benzene, THF, and dichloromethane. As the polymer adsorbed to the GPC column when THF was used as an eluant, it was analyzed using a THF solution containing 2.0% v/v of triethylamine. The GPC analysis indicated that the polymer possessed a molecular weight of $M_n = 4.6 \times 10^3$ and a PDI of 1.30, corresponding to ≈ 13 repeat units in each polymer chain. Notably, when a polystyrene (PS) standard ($M_p = 3600$, PDI $= 1.04$) was analyzed on the same instrument by the same method, its molecular weight and polydispersity index were $M_n = 4.5 \times 10^3$ and 1.18,



Scheme 9.

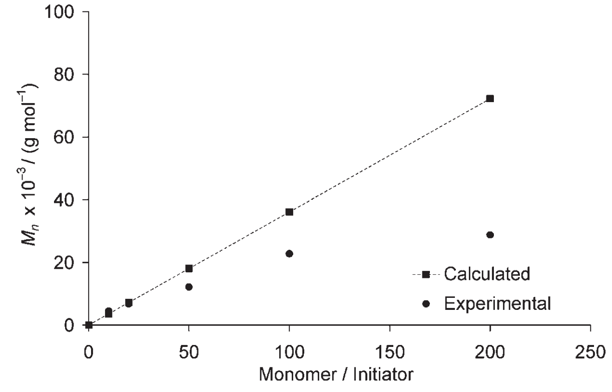


Figure 2. Variation of molecular weight of polymer **21** with monomer/initiator ratio, [M]/[I], as calculated (■) and obtained experimentally (●).

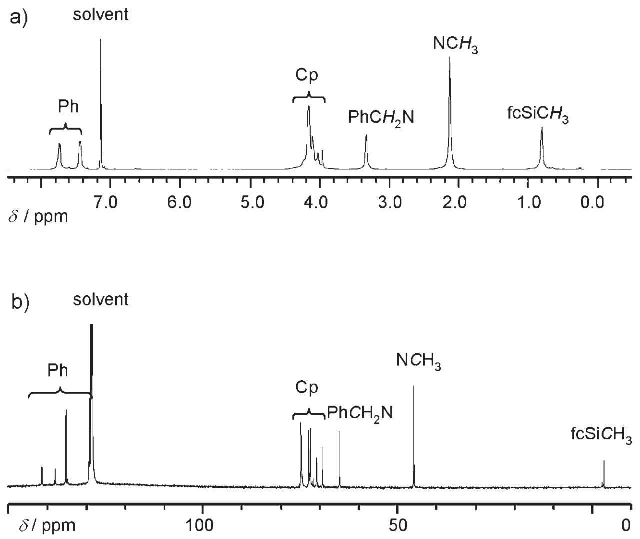


Figure 3. a) ^{1}H (400 MHz) and b) ^{13}C (100 MHz) NMR spectra of polymer **21** in C_6D_6.

respectively. The GPC result of the PS standard suggested that the polydispersity of PFS **21** was likely to be much smaller than 1.30. End-group analysis by using ^{1}H NMR spectroscopy indicated that the number of monomeric units is approximately 13, which is comparable to that obtained from the GPC analysis.

By varying the monomer/initiator ratio from 10 to 200, polymer **21** have been obtained with molecular weight ranging from 4.6×10^3 to 2.9×10^4 (Table 2). However, good molecular weight control and narrow polydispersity were only achieved for polymers which possess up to 20 monomeric units. At a higher monomer/initiator ratio (50:1), PFS **21** was obtained with large polydispersity and molecular weights that deviate significantly from the theoretical values (Figure 2).[38]

PFS **21** was characterized by using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Figure 3). For polymers that have short chain length, the ^{1}H NMR spectrum showed a distinct chemical shift at $\delta=3.96$ ppm, corresponding to the protons of the capping η^5-C_5H_5 group at the ferrocenyl end of the polymer chain. This allows estimation of the number-average degree of polymerization ($DP_{n,NMR}$) for polymers that have repeat units of up to 100 by using end-group analysis through integration of the Cp protons in the end group and in the main-chain ferrocenyl moieties ($\delta=4.00$–4.28 ppm). In the ^{13}C NMR spectrum, a downfield shift was detected for the *ipso*-carbon from $\delta=32.7$ ppm in monomer **20** to $\delta=70.8$ ppm in polymer **21** as a result of the release of ring-strain in the monomer. The η^5-C_5H_5 carbons at the ferrocenyl chain end were again clearly observed at $\delta=69.2$ ppm. The ^{29}Si NMR spectrum of **21** exhibited one signal at $\delta=-11.5$ ppm, which was in accordance with the assigned structure.

Table 2. Summary of data for polymer **21** synthesized by PROP.

Sample	[M]/[I][a]	$DP_{n,NMR}$[b]	$M_{n,calc}$[c]	$M_{n,GPC}$	PDI[d]	*t* [h]	Yield of PFS **21** [%]	Yield of (+)PFS **22** [%]
a	10	13	3610	4600	1.30	3	70	93
b	20	20	7220	6800	1.20	4	62	70
c	50	60	18050	12200	1.45	4	58	90
d	100	80	36100	22800	1.65	5	48	82
e	200	–	72200	28800	2.61	6	52	77

[a] [M]/[I] denotes monomer:initiator ratio. [b] Values determined by ^{1}H NMR integration of Cp polymer protons relative to the Cp end-group protons. [c] Cp end groups are not included. [d] Given by M_w/M_n from GPC analysis.

Quaternization of 21—synthesis and characterization of cationic polyelectrolyte 22: In a procedure analogous to the synthesis of cationic PFS **7** from dimethylaminopropynyl PFS **15**, the dimethylamino groups in polymer **21** were quaternized in the presence of dimethyl sulfate to give the desired cationic PFS **22** as an orange powder (Scheme 9). This polyelectrolyte was soluble in water, methanol, and aqueous NaCl solutions. The solutions remained clear and stable over a long period of time (i.e. more than half a year) under ambient conditions.

The cationic PFS **22** in deuterated methanol was characterized by using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Figure 4). In the ^{1}H spectrum, the ammonium methyl protons exhibited a resonance at $\delta = 3.11$ ppm, which was shifted significantly downfield from the dimethyl protons in PFS **21** ($\delta = 2.12$ ppm) as a result of the quaternization. The same downfield shift was also observed for the methylene protons adjacent to the nitrogen atom from $\delta = 3.33$ ppm in **21** to $\delta = 4.59$ ppm in the cationic polymer. In addition, the absence of the dimethylamino proton signals in the ^{1}H spectrum of **22** confirmed the successful quaternization of polymer **21**. The ^{13}C and ^{29}Si NMR of the polymer were also consistent with the assigned structure.

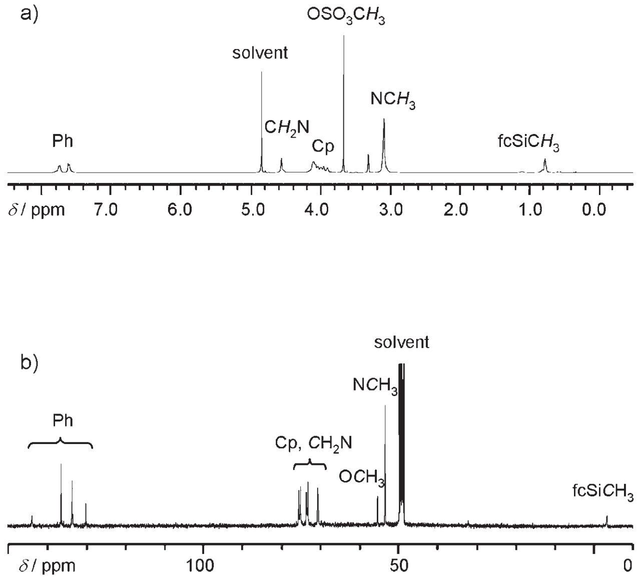


Figure 4. a) ^{1}H (400 MHz) and b) ^{13}C (100 MHz) NMR spectra of polymer **22** in CD_3OD.

Layer-by-layer self-assembly of PFSs 6 and 22—study of the molecular-weight effect on the structure and optical properties of LbL films: The technique of LbL self-assembly has been widely utilized as a practical method for surface modification and patterning as well as manufacturing of thin film devices due to its simplicity and versatility.[2,3] While a wide variety of polyelectrolytes have been successfully assembled for many practical applications, the uncontrolled architectures of these polymers pose a significant challenge to the fundamental studies of the structure and property of the multilayer films, as uncontrolled polymer molecular weight and broad molecular-weight distributions can sometimes make interpretation of experimental results difficult.[39] Polyelectrolytes that have large uncontrolled molecular weights can also complicate LbL assembly in highly confined spaces with narrow openings such as micro- and nanochannels as well as photonic crystals. In this work, we assembled LbL films using polycation **22** and polyanion **6**, which possess controlled molecular weight and narrow polydispersity, and our preliminary study indicated that the molecular weight of these polyelectrolytes had a significant influence on the bilayer thickness and refractive index (RI) of these films.

The LbL assembly was carried out by sequentially dipping a silicon substrate into the aqueous solutions of (+)PFS **22** ($DP_n \approx 13$, $M_n \approx 6.4 \times 10^3$) and (−)PFS **6** ($DP_n \approx 10$, $M_n \approx 4.4 \times 10^3$). The ionic strength of both solutions was maintained at a salt concentration of 0.1 M NaCl. To minimize the effect of molecular weight distribution, polyelectrolytes that have a polydispersity index of less than 1.30 were used. Multilayer films of 5, 10, 20, 30, and 40 bilayers of PFS polyelectrolytes were thus constructed, with each bilayer consisting of one (+)PFS and one (−)PFS monolayer.

The thickness and refractive index of these well-defined LbL films were examined by using ellipsometry measurements. The linear relationship between film thickness and bilayer number indicated a regular film growth in the LbL assembly (Figure 5a), with the thickness of each bilayer estimated to be ≈1.3 nm. The refractive index of each film was measured in the visible-near IR region of $\lambda = 400$–1400 nm (Figure 5b), with the RI value determined as 1.68 at $\lambda = 600$ nm. This is comparable to the refractive indices of spin-

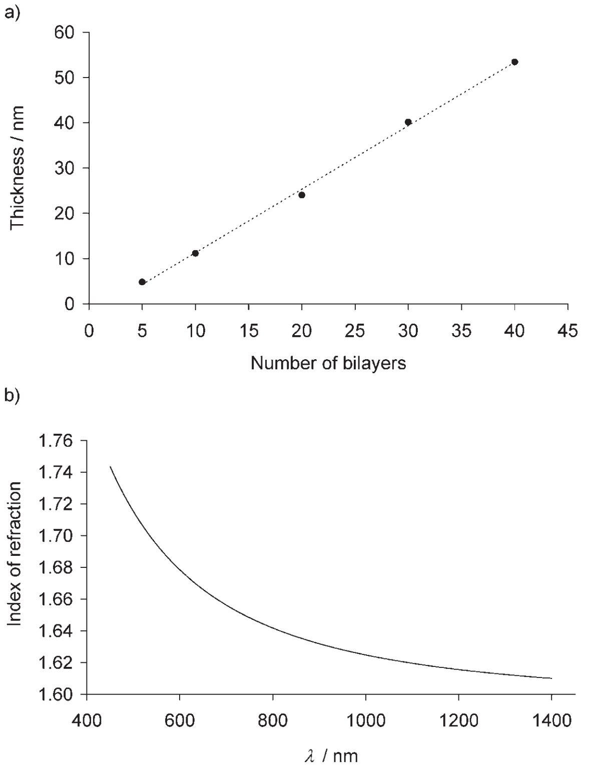


Figure 5. a) Plot of LbL film thickness versus bilayer number. b) Dispersion of the index of refraction for the LbL structures.

cast polymer films from PFSs with analogous structures.[40] Our study also indicated that the index of refraction did not change significantly with respect to the multilayer thickness.

The aforementioned results, are significantly different from our previous work in which LbL films have been assembled from PFS polyelectrolytes with uncontrolled high molecular weight ($M_w \approx 10^5$–10^6) and polydispersity (PDI > 1.8). For example, films assembled from (+)PFS **17**[41] and (−)PFS **6**, which have molecular weight in the order of 10^5, have been found to exhibit a bilayer thickness of 4.8 nm, significantly larger than that of the low molecular-weight films.[42] In addition, the refractive index of these films was determined to be 1.52 at $\lambda = 600$ nm, much lower than that of the low molecular-weight LbL films or spin-cast films of analogous structures.

The difference between the two groups of LbL films suggests a more condensed multilayer structure in the well-defined films assembled from low molecular-weight PFSs. LbL assembly is generally considered as a multistep kinetic process in which the coiled chains of polyelectrolytes first adsorb onto a substrate surface and then relax to form more extended chains.[2,3] In the case of low molecular-weight PFSs, it may be difficult for the short polyelectrolyte chains to adopt coiled conformations in aqueous solutions, owing to steric restrictions of the bonds and electrostatic interactions of the partially shielded ionic groups.[43] It is suspected that PFS chains may deposit onto the substrate surface in relatively extended conformations, which can lead to compact multilayers with fewer loops and voids that contain air and water, thus giving rise to thinner bilayer thickness and higher refractive index. Further detailed study of the effect of polymer molecular weight on the LbL assembly of multilayer films is currently underway and will be reported in the near future.

Conclusion

We have achieved the facile and reliable synthesis of the first water-soluble metallopolyelectrolytes with transition metals in the main chain, which possess controlled molecular weight and narrow polydispersity. These macromolecules have been obtained through the photolytic ROP of amino-functionalized [1]ferrocenophanes followed by further derivatizations. The polyelectrolytes are readily soluble in water and aqueous NaCl solutions, with **6** and **22** exhibiting stability in aqueous NaCl solutions over a long period of time. PFSs **6** and **22** have been utilized in the layer-by-layer self-assembly of multilayer films, and their controlled structures allow fundamental studies of LbL films in a more precise fashion. Our preliminary results indicate that films made from low molecular-weight PFSs are considerably thinner and possess higher refractive index than those made from high molecular-weight PFSs. This suggests that the structure and optical properties of LbL thin films can be tuned by varying polymer chain length, which may have significant implications in the manufacturing of thin-film devices, coatings, or gradients with defined dimensions and desired photonic properties. Further detailed investigation of multilayer films as a function of PFS molecular weight, as well as LbL self-assembly of water-soluble PFSs in confined spaces, will be reported in the near future.

Experimental Section

Materials: All chemicals were purchased from Aldrich and used as received unless otherwise specified. Compounds $HC{\equiv}CCH_2N(SiMe_2CH_2)_2$,[26] $[fcSiCl_2]$ (**8**),[34] fcSiMeCl (**12**),[34] and polyelectrolyte $[\{fcSiMe(o\text{-}C_6H_4CH_2NMe_3OSO_3Me)\}_n]$ (**17**)[24] ($M_w \approx 10^5$) were synthesized according to literature procedures. Solvents were dried according to standard methods. Aqueous polyelectrolyte solutions were prepared by using deionized water (18.2 MΩ cm). Si(111) substrates ($2\times1\ cm^2$) were cut from 3″ polished wafers (International Wafer Service). Si substrates were sputtered with a 100 Å Cr adhesion layer followed by a 1000 Å Au layer.

Equipment: All manipulations of air-sensitive materials were performed under nitrogen atmosphere either in an MBraun glovebox or by using standard Schlenk line techniques. ^1H, ^{13}C NMR and ^{29}Si spectra were recorded on Varian spectrometers (Unity 400, Gemini 300 or Mercury 300) and referenced to residual protonated solvent (^1H) or deuterated solvent (^{13}C) unless otherwise specified. Mass spectra were obtained with the use of a VG 70–250S mass spectrometer operating in electron impact (EI) mode. Molecular weights were estimated by using gel permeation chromatography (GPC) by using a Waters Associates 2690 separation module equipped with a column heater, in-line degasser, a High Performance Liquid Chromatography (HPLC) pump, and an autosampler. The separation module was equipped with a Waters 410 differential refractometer as the concentration detector and, connected in parallel, a Viscotek T60A dual detector consisting of a right-angle laser light scattering detector with a laser source of 670 nm and a four-capillary differential viscometer. Software from Viscotek was used to analyze the data. Columns from Polymer Laboratories with pore sizes of 5×10^2, 1×10^4, and 1×10^5 Å were used with THF as the eluant unless otherwise specified at a flow rate of 1.0 mL min^{-1}. Polystyrene standards purchased from Aldrich and Viscotek were used for calibration.[44]

LbL assembly of PFS multilayers: The concentrations of the polyelectrolyte solutions were 10 mM PFS, based on the respective monomer repeat units. Each solution was made in 0.1 M NaCl and filtered through a 0.45 μm syringe filter prior to use. The substrates were alternately placed in the PFS polyanion and polycation solutions for 10 min, rinsed with deionized water through three immersions for 4 min each after each exposure to polyelectrolyte, and finally dried with a gentle stream of compressed air.

Ellipsometry measurements: Ellipsometric measurements were obtained by using a SOPRA GES-5 variable-angle spectroscopic ellipsometer. For each sample, ellipsometry spectra were obtained at angles of incidence of 70 and 75 degrees. Using known values of the dielectric function of Au substrate, and by varying film thickness and refractive index of the LbL layer, the experimental data were fit to a model, which also included a rough layer in the order of 1 nm. To improve fits, the LbL layer was modeled as a film with 5–10 % thickness-nonuniformity.

Synthesis of $[(fcSiMe\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\})_n]$ (5), $[(fcSi\{C{\equiv}CCH_2N(SiMe_2CH_2)_2\}_2)_n]$ (11), $[\{fcSiMe(C{\equiv}CCH_2NMe_2)\}_n]$ (15): In a typical procedure, $Na[C_5H_5]$ (0.024 mL of 2.0 M solution in THF, 0.047 mmol) was added in the absence of light to a solution of sila[1]ferrocenophane **3** (200 mg, 0.472 mmol) in THF (2 mL). The solution was irradiated with UV/Vis light and stirred for 2.5 h at 5 °C. The reaction was terminated with a few drops of degassed ethanol, concentrated, precipitated into methanol, and dried under high vacuum to afford polymer **5** as an orange gummy solid (145 mg, 0.342 mmol, 73 %). ^1H NMR (300 MHz, C_6D_6): δ = 0.25, 0.27 (12H; $NSi(CH_3)_2$), 0.79 (s, 4H; $NSiCH_2$), 0.82 (s, 3H; $fcSiCH_3$), 3.64, 3.66, 3.68 (2H; NCH_2), 4.21 (s, η^5-C_5H_5Fe), 4.23–4.72 ppm (m, 8H;

Cp); ^{13}C NMR (75 MHz, C_6D_6): $\delta=-0.09$ (fcSi*C*H$_3$), 0.3 (NSi(*C*H$_3$)$_2$), 8.8 (NSi*C*H$_2$), 32.4 (N*C*H$_2$), 69.5 (η^5-*C*$_5$H$_5$Fe), 69.83, 69.86 (*ipso*-Cp), 73.19, 73.22, 74.6, 74.8 (Cp), 85.1 (Si*C*≡CCH$_2$), 109.7 ppm (SiC≡*C*CH$_2$); GPC: $M_n=6.3\times10^3$, PDI = 1.10.

[(fcSi{C≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$}$_2$)$_n$] (***11***): ^{1}H NMR (400 MHz, C_6D_6): $\delta=$ 0.22, 0.25, 0.27, 0.28, 0.29 (24 H; NSi(C*H*$_3$)$_2$), 0.79, 0.81, 0.82 (8 H; NSiC*H*$_2$), 3.67, 3.66, 3.68 (4 H; NC*H*$_2$), 4.35 (s, η^5-C$_5$*H*$_5$Fe), 4.69, 4.93 ppm (s, 8 H; Cp); ^{13}C NMR (100 MHz, C_6D_6): $\delta=0.29$, 0.37 (NSi(*C*H$_3$)$_2$), 8.8 (NSi*C*H$_2$), 32.4 (N*C*H$_2$), 67.7 (*ipso*-Cp), 69.9 (η^5-*C*$_5$H$_5$Fe), 72.2, 74.3, 74.7, 75.3 (Cp), 82.8 (Si*C*≡CCH$_2$), 109.9 ppm (SiC≡*C*CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6): $\delta=-45.8$, 14.9 ppm; GPC: $M_n=4.9\times10^3$, PDI = 1.13.

[{fcSiMe(C≡CCH$_2$NMe$_2$)}$_n$] (***15***): ^{1}H NMR (300 MHz, C_6D_6): $\delta=0.23$ (s, fcSiC*H*$_3$(C$_5$H$_5$)), 0.75, 0.78 (3 H; fcSiC*H*$_3$fc), 2.27 (s, 6 H; NC*H*$_3$), 3.23 (s, 2 H; NC*H*$_2$), 4.18 (s, η^5-C$_5$*H*$_5$Fe), 4.20–4.67 ppm (m, 8 H; Cp); ^{13}C NMR (100 MHz, C_6D_6): $\delta=0.10$, 0.12, 0.37 (fcSi*C*H$_3$), 44.7 (N*C*H$_3$), 49.6 (N*C*H$_2$), 69.5 (η^5-*C*$_5$H$_5$Fe), 69.9 (*ipso*-Cp), 71.87, 71.93, 73.2, 73.3, 74.1, 74.5, 74.6, 74.89, 74.95 (Cp), 88.6 (Si*C*≡CCH$_2$), 103.9 ppm (SiC≡*C*CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6): $\delta=-24.7$ ppm; GPC: $M_n=3.4\times10^3$, PDI = 1.08.

Synthesis of [{fcSiMe(C≡CCH$_2$NMe$_3$OSO$_3$Me)}$_n$] (7)

Procedure A: Diisopropylethylamine (1.03 mL, 5.90 mmol) followed by dimethyl sulfate (0.45 mL, 4.72 mmol) were added to a solution of PFS **5** (500 mg, 1.18 mmol) in a mixture of THF (20 mL) and methanol (5 mL) at 25 °C. As the reaction proceeded, additional methanol was added to dissolve some of the cationic polymer which precipitated out of the solution. After seven days of reaction at room temperature, the solvents were removed on a rotavap and the residue was dissolved in a small amount of methanol prior to precipitation in THF. Suction filtration followed by drying under high vacuum afforded the cationic polymer **7** as an orange powder (270 mg, 0.620 mmol, 53 %).

Procedure B: Diisopropylethylamine (0.19 mL, 1.09 mmol) followed by dimethyl sulfate (0.10 mL, 1.09 mmol) were added to a solution of PFS **15** (168 mg, 0.543 mmol) in a mixture of THF (6 mL) and methanol (1.5 mmol). The reaction mixture was stirred at 25 °C for 8 h. Removal of the solvents on a rotavap followed by precipitation in THF afforded cationic polymer **7** as an orange powder (154 mg, 0.353 mmol, 65 %). ^{1}H NMR (400 MHz, D_2O): $\delta=0.77$ (br, 3 H; fcSiC*H*$_3$fc), 3.22 (s, br, 9 H; NC*H*$_3$), 3.74 (s, 3 H; OSO$_3$C*H*$_3$), 4.00–4.73 ppm (m, br, 10 H; Cp and C*H*$_2$N); ^{13}C NMR (100 MHz, D_2O, $\delta_{\mathrm{ref(acetone)}}=30.2$ ppm): $\delta=0.2$ (fcSi*C*H$_3$), 52.7 (N*C*H$_3$), 55.1 (OSO$_3$*C*H$_3$), 56.8 (N*C*H$_2$), 68.9 (*ipso*-Cp), 72.9, 73.9 (Cp), 94.4 (Si*C*≡CCH$_2$), 96.0 ppm (SiC≡*C*CH$_2$).

Synthesis of [fcSi{C≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$}$_2$] (10): *n*BuLi (8.84 mL of 1.6 M solution in hexanes, 14.1 mmol) was added dropwise to a solution of protected propargylamine HC≡CCH$_2$N(SiMe$_2$CH$_2$)$_2$[26] (2.86 g, 14.5 mmol) in diethyl ether (40 mL) at −78 °C. After 5 min of stirring, the cold bath was removed and the reaction mixture was stirred for ≈10 min before it was added slowly through a canula to a solution of dichloroferrocenophane **8** (2.0 g, 7.07 mmol) in diethyl ether (50 mL) at −78 °C. The reaction mixture was slowly warmed to 25 °C and stirred overnight. Filtration of the reaction mixture followed by removal of the solvents under high vacuum gave a dark red residue which was dissolved in hexanes (50 mL) and filtered again to remove any remaining lithium salt. Evaporation of hexanes (≈25 mL) followed by recrystallization at −35 °C gave **10** as a red solid (0.980 g, 1.62 mmol, 23 %). ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.21$ (s, 24 H; NSi(C*H*$_3$)$_2$), 0.75 (s, 8 H; NSiC*H*$_2$), 3.53 (s, 4 H; NC*H*$_2$), 4.43, 4.52 ppm (m, 8 H; Cp); ^{13}C NMR (100 MHz, C_6D_6): $\delta=-0.28$ (NSi(*C*H$_3$)$_2$), 8.3 (NSi*C*H$_2$), 28.8 (N*C*H$_2$), 31.9 (*ipso*-Cp), 75.4, 78.5 (Cp), 79.4 (Si*C*≡CCH$_2$), 110.8 ppm (SiC≡*C*CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6): $\delta=-55.6$, 15.3 ppm; HRMS for $C_{28}H_{44}FeN_2Si_5$ calcd: 604.1700; found: 604.1687.

Synthesis of [fcSiMe(C≡CCH$_2$NMe$_2$)] (14): *n*BuLi (6.07 mL of 1.6 M solution in hexanes, 9.71 mmol) was added dropwise to a solution of 3-dimethylamino-1-propyne (1.08 mL, 10.0 mmol) in diethyl ether (70 mL) at −78 °C. After 5 min of stirring, the cold bath was removed and the white suspension was stirred for ≈3 min before it was cooled again to −78 °C. A solution of chloromethylferrocenophane **12** (2.50 g, 9.52 mmol) in diethyl ether (50 mL) through a canula was added slowly to this suspension. The reaction mixture was slowly warmed to 25 °C and stirred overnight. Filtration of the reaction mixture followed by removal of the solvents under high vacuum gave a dark red residue, which was dissolved in hexanes and filtered again to remove any remaining lithium salt. Recrystallization in hexanes at −35 °C followed by sublimation at 70–75 °C gave **14** as a red crystalline solid (1.86 g, 6.01 mmol, 63 %). ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.57$ (s, 3 H; fcSiC*H*$_3$), 2.20 (s, 6 H; NC*H*$_3$), 3.18 (s, 2 H; NC*H*$_2$), 3.89, 4.38, 4.44, 4.51 ppm (m, 8 H; Cp); ^{13}C NMR (75 MHz, C_6D_6): $\delta=-2.6$ (fcSi*C*H$_3$), 31.0 (*ipso*-Cp), 44.4 (N*C*H$_3$), 49.3 (N*C*H$_2$), 75.0, 77.0, 78.5, 78.6 (Cp), 85.6 (Si*C*≡CCH$_2$), 104.6 ppm (SiC≡*C*CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6): $\delta=-28.7$ ppm.

Synthesis of [fcSiMe(*p*-C$_6$H$_4$CH$_2$NMe$_2$)] (20): 4-Bromobenzyldimethylamine (**18**) was prepared according to a modified literature procedure.[36] Dimethylamine (50 mL of 2.0 M solution in THF, 100 mmol) and diisopropylethylamine (17.4 mL, 100 mmol) were added dropwise to a solution of 4-bromobenzyl bromide (16.7 g, 66.7 mmol) in benzene (100 mL) at 5 °C . The white suspension was stirred for 1 h at 5 °C and then for 2 days at 25 °C. Filtration of the reaction mixture followed by thorough washing of the white solid with benzene (30 mL × 3) gave a combined organic solution which was concentrated on a rotavap. Further filtration of the residual white solid followed by vacuum distillation of the crude product afforded 4-bromobenzyldimethylamine (**18**) as a clear colorless liquid (7.68 g, 35.9 mmol, 54 %) which was used in the following step. *n*BuLi (9.31 mL of 1.6 M solution in hexanes, 14.9 mmol) was quickly added dropwise to a solution of 4-bromobenzyldimethylamine (**18**) (3.25 g, 15.2 mmol) in diethyl ether (25 mL) at −78 °C. The yellow solution was stirred for ≈2–3 min before a solution of chloromethylferrocenophane **12** (4.00 g, 15.2 mmol) in diethyl ether (25 mL) was added dropwise quickly through a canula. The reaction mixture was slowly warmed to 25 °C during a three hour period. Removal of the solvents under high vacuum gave a dark red residue, which was dissolved in hexanes (80 mL) and filtered to remove the lithium chloride salt. Repeated recrystallization at −55 °C gave **20** as a red crystalline solid (2.20 g, 6.09 mmol, 40 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta=0.58$ (s, 3 H; fcSiC*H*$_3$), 2.12 (s, 6 H; NC*H*$_3$), 3.31 (s, 2 H; NC*H*$_2$), 4.03, 4.06, 4.39, 4.44 (m, 8 H; Cp), 7.48 (d, $J=7.8$ Hz, 2 H; Ph), 7.96 ppm (d, $J=8.0$ Hz, 2 H; Ph); ^{13}C NMR (75 MHz, C_6D_6): $\delta=-2.1$ (fcSi*C*H$_3$), 32.7 (*ipso*-Cp), 45.9 (N*C*H$_3$), 64.9 (N*C*H$_2$), 76.4, 77.1, 78.3, 78.4 (Cp), 129.5, 134.5, 134.9, 142.7 ppm (Ph). ^{29}Si NMR (79 MHz, C_6D_6): $\delta=-8.2$ ppm.

Synthesis of [{fcSiMe(*p*-C$_6$H$_4$CH$_2$NMe$_2$)}$_n$] (21): Na[C$_5$H$_5$] (0.042 mL of 2.0 M solution in THF, 0.083 mmol) in the absence of light was added to a solution of sila[1]ferrocenophane **20** (300 mg, 0.830 mmol) in THF (2 mL). The solution was irradiated with UV/Vis light and stirred for 3 h at 5 °C. The reaction was terminated with a few drops of degassed ethanol, concentrated, precipitated into methanol, and dried under high vacuum to afford polymer **21** as an orange gummy solid (210 mg, 0.581 mmol, 70 %). ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.79$ (s, 3 H; fcSiC*H*$_3$), 2.12 (s, 6 H; NC*H*$_3$), 3.33 (s, 2 H; NC*H*$_2$), 3.96 (s, η^5-C$_5$*H*$_5$Fe), 4.00–4.28 (m, 8 H; Cp), 7.46 (d, $J=8.0$ Hz, 2 H; Ph), 7.75 ppm (d, $J=8.0$ Hz, 2 H; Ph); ^{13}C NMR (100 MHz, C_6D_6): $\delta=-2.9$, −2.4 (fcSi*C*H$_3$), 45.9 (N*C*H$_3$), 64.9 (N*C*H$_2$), 69.2 (η^5-*C*$_5$H$_5$Fe), 70.75, 70.80 (*ipso*-Cp), 71.5, 71.9, 72.4, 72.7, 72.8, 74.6, 74.7, 74.8 (Cp), 129.0, 135.0, 137.8, 141.2 ppm (Ph); ^{29}Si NMR (79 MHz, C_6D_6): $\delta=-11.5$ ppm; GPC (2.0 % v/v Et$_3$N in THF as eluant): $M_n=4.6\times10^3$, PDI = 1.30 (under the same condition, standard PS with $M_p=3600$ and PDI = 1.04 was detected with a molecular weight of $M_n=4.5\times10^3$ and PDI = 1.18).

Synthesis of [{fcSiMe(*p*-C$_6$H$_4$CH$_2$NMe$_3$OSO$_3$Me)}$_n$] (22): Diisopropylethylamine (0.22 mL, 1.25 mmol) and dimethyl sulfate (0.12 mL, 1.25 mmol) were added to a solution of PFS **21** (180 mg, 0.50 mmol) in THF (2 mL) at 25 °C. Methanol (4 mL) was added to dissolve the precipitate formed in the reaction mixture and the clear orange solution was stirred for 2 h. After removal of the solvents on a rotavap, the residue was dissolved in a small amount of methanol and precipitated in acetone. The precipitate was redissolved in a small amount of methanol and precipitated in THF. Suction filtration followed by drying under high vacuum afforded polymer **22** as an orange powder (225 mg, 0.46 mmol, 93 %). ^{1}H NMR (400 MHz, CD_3OD): $\delta=0.79$ (s, 3 H; fcSiC*H*$_3$), 3.11 (s, 9 H; NC*H*$_3$), 3.69 (s, 3 H; OSO$_3$C*H*$_3$), 3.90–4.21 (m, 8 H; Cp), 4.59 (s, 2 H; NC*H*$_2$), 7.64 (d, $J=7.2$ Hz, 2 H; Ph), 7.78 ppm (br, 2 H; Ph); ^{13}C NMR

(100 MHz, CD_3OD): $\delta = -3.4$ (fcSiCH_3), 53.4 (NCH_3), 55.3 (OSO_3CH_3), 70.4–70.7 (NCH_2, η^5-C_5H_5Fe, *ipso*-Cp), 73.1, 73.5, 75.0, 75.4 (Cp), 129.9, 133.4, 136.2, 143.7 ppm (Ph); ^{29}Si NMR (79 MHz, CD_3OD): $\delta = -11.1$ ppm.

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