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Electrochemically Triggered Surface Deposition of Polyelectrolytes

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Supporting Information

ABSTRACT: An electrochemical approach to surface deposition of polyelectrolytes on self-assembled monolayers is presented. This deposition process can be triggered facilely by a potential bias, which oxidizes ferrocene moieties included in the self-assembled monolayer to ferrocenium, whose charge compensation is fulfilled by polyelectrolytes and associated counterions. This approach is quite general, affording quantitative deposition of both polyanions and polycations with a wide range of chemical identities (synthetic polymers, peptides, and DNA) and molecular weights $(10^3-10^7 \text{ Da as tested})$. Conventional layer-by-layer polyelectrolyte deposition can be straightforwardly combined with this method to produce electroactive polymer films. Several techniques, including voltammetry, fluorescence spectroscopy, contact angle analysis, electrochemical quartz crystal microbalance, and atomic force microscopy, were employed to characterize the deposition processes. A detailed discussion on the involved deposition mechanisms is also presented.



INTRODUCTION

This article reports a new approach to polyelectrolyte deposition on self-assembled monolayer (SAM) surfaces that can be triggered facilely by a potential bias. When applied, this bias drives the oxidation of ferrocene (Fc) moieties on the SAM to ferrocenium (Fc^+), whose charge compensation in this particular case is fulfilled by polyelectrolytes and associated counterions present in the surroundings. This approach is quite general, enabling quantitative deposition of both polyanions and polycations with a wide range of chemical identities (synthetic polymers, peptides, and DNA) and molecular weights $(10^3 - 10^7)$ Da). Besides its practical implications, this work also illustrates the possibility and potential benefits of conducting electrochemical processes under unconventional conditions-here, use of polyelectrolytes in place of small ions to maintain interfacial charge balance.

Like many other truly useful technologies, gold-anchored alkanethiol SAMs¹ are simple to operate and yet rich in offering. Through their distal end, a variety of functionalities can be attached to these alkanethiols, which, when similarly assembled, yield well-defined surfaces on which diverse chemistries can be launched. Among these are ferrocene-terminated SAMs, which have served not only as an invaluable model system for probing fundamental electron transfer processes²⁻⁴ but also a flexible platform for biosensing,^{5,6} electroactuation,⁷ and molecular photovoltaics.^{8,9} On the other hand, alkanethiols terminated with amine and carboxylic groups readily afford charged SAMs, which, among other possibilities, provide excellent starting surfaces for layer-by-layer polyelectrolyte deposition.^{10,11} This fruitful integration has led to electroactive polymer/protein ^{2,13} as films displaying robust electrochemical communication,¹ well as redox-doped polyelectrolyte multilayers whose thickness

and mechanical properties can be electrochemically manipulated.14,15

This work introduces a new type of SAM/polyelectrolyte integration that is electrochemically initiated and controlled. In relation to existing systems, this approach combines the following features: (1) facile polymer deposition that can be accomplished in a matter of seconds; (2) quantitative deposition, according to ferrocene density prepared into the SAMs; (3) broad applicability, to both anionic and cationic polyelectrolytes, either synthetic or natural, in a wide molecular weight range; and (4) ready coupling to conventional layer-bylayer polyelectrolyte deposition to yield electroactive polymer composite films. All these features, importantly, can be obtained from the same starting surfaces-ferrocene-terminated SAMs. Several techniques, including voltammetry, fluorescence spectroscopy, contact angle analysis, electrochemical quartz crystal microbalance, and atomic force microscopy, were employed to characterize the deposition processes. A detailed discussion on the involved deposition mechanisms is also presented.

EXPERIMENTAL SECTION

Reagents. 11-Ferrocenyl-1-undecanethiol (Fc-C11SH), 1-dodecanethiol (C12SH), poly(acrylic acid sodium salt), poly(allylamine hydrochloride), poly(fluorescein isothiocyanate allylamine hydrochloride) with a polymer to fluorophore mole ratio of 50:1, DNA sodium salt from calf thymus, and sodium perchlorate hydrate (99.99% trace metal basis) were products of Sigma-Aldrich (St. Louis, MO). Poly(L-lysine hydrochloride) and poly(L-glutamic acid sodium salt) were obtained from Alamanda Polymers (Huntsville, AL). 5'-Fluorescein-labeled poly(adenine) 25-mer was obtained from Inte-

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^aPoly(allylamine HCl) only.

grated DNA Technologies, Inc. (Coralville, IA). The structure and molecular weight of these polymers are listed in Table 1. Deionized water of 18.2 M Ω ·cm (Millipore) was used in preparing all aqueous solutions as well as in all rinsing steps.

Formation of Self-Assembled Monolayers. Self-assembled monolayers (SAMs) of Fc-C11SH, either pure or mixed 1:1 (mole ratio) with C12SH, were formed on three types of gold-coated substrates depending on the intended use. For voltammetric and water contact angle characterization, the substrates were prepared in-house by sputtering gold onto chromium-coated silicon wafers (Au thickness: \sim 1000 nm). The other two substrates were commercially obtained: semitransparent gold-coated microscope slides (Au thickness: 10 nm, Sigma-Aldrich) for fluorescence spectroscopy and atomic force microscopy and gold-coated quartz crystal wafers with a Cr adhesion layer (diameter: 1 in., Stanford Research System, Sunnyvale, CA) for quartz crystal microbalance. Right before their incubation in thiol solutions, these substrates were immersed in a piranha solution (3:1 v/v)mixture of concentrated H_2SO_4 and H_2O_2 30 wt % aqueous solution) for either 15 (for the gold-coated Si wafers) or 3 min (for the other two substrates), thoroughly rinsed with deionized water and ethanol, and then dried under N2. Thus, cleaned dry substrates were immediately immersed in an ethanol solution dissolved either with 0.5 mM Fc-C11SH and C12SH each (for mixed Fc SAMs) or with 1.0 mM Fc-C11SH alone (for pure Fc SAMs). The incubation was allowed to proceed for 16-18 h in the dark, after which the substrates were thoroughly rinsed with methanol to remove excess thiols on surface, then rinsed with deionized water, and finally dried under N2. These freshly prepared SAMs are immediately subjected to their next treatments as specified below.

Electrochemical Treatments and Characterization. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used in this work to (1) initiate polyelectrolyte deposition on Fc SAMs and (2) electrochemically characterize the Fc SAMs before/after the deposition step. These measurements were performed in homemade Teflon cells housing SAM-covered gold substrates as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl in saturated KCl solution as the reference electrode and are operated by a PC-controlled potentiostat (CHI 910B, CH Instruments, Austin, TX) with a potential scan rate of 100 mV/s. In the order of operation, a given SAM is typically treated with three separate voltammetric scans: (1) a CV scan in 0.1 M NaClO₄, (2) an LSV or a CV scan in a 1.0 mM (polymer concentration) aqueous solution of a polyelectrolyte, and (3) another CV scan back in 0.1 M NaClO₄. In between scans, the solution occupying the electrochemical cell was thoroughly exchanged out first with deionized water and then with the medium intended for the next

scan. To ensure reproducibility, it is critical to keep the SAM immersed in liquid during the entire time of these voltammetric runs.

Water Contact Angle Measurement. A Ramé-Hart model 200 automated goniometer (Succasunna, NJ) was used to measure the water contact angles of Fc-C11SH/C12SH mixed SAMs at room temperature. The Ramé-Hart DROPimage Standard software was used to collect images and analyze the obtained angles. Prior to a measurement, a SAM was first LSV-treated in either DI water alone or a 1.0 mM polyelectrolyte aqueous solution, thoroughly washed with deionized water, and then dried under N₂. In each case, a measurement was promptly taken after a 4 μ L deionized water droplet was gently placed onto the SAM.

Electrochemical Quartz Crystal Microbalance (EQCM). EQCM measurements were carried out on a Stanford Research Systems QCM analyzer with a 5 MHz crystal oscillator (Model: QCM25, Sunnyvale, CA) at room temperature. The quartz crystals used here are polished quartz wafers of 1 in. diameter with circular gold electrodes coated on both sides, which are first grafted with a 1:1 Fc-C11SH/C12SH mixed SAM as described above. The SAM-coated crystal was subsequently mounted on the QCM crystal holder, and its solution-facing electrode was used as the working electrode in a threeelectrode configuration together with a Pt-wire counter electrode and a Ag/AgCl reference electrode (in saturated KCl). To do so, a PCcontrolled potentiostat (CHI 910B, CH Instruments) was connected to the QCM crystal holder via the crystal face bias connector of the QCM25 crystal controller. This setup enables simultaneous monitoring of the QCM frequency shift and current on the working electrode (crystal) as a function of the applied potential. The potential is fed by the potentiostat in the form of 10 consecutive CV scans between 0.1 and 0.8 V; scan rate: 100 mV/s.

Fluorescence Spectroscopy. Fluorescence emission spectra of fluorescein-conjugated polyelectrolytes deposited on semitransparent gold-coated microscope slides were acquired on a PI Acton spectrometer (Spectra Pro SP 2356, Acton, NJ) equipped with a CCD camera (PI Acton PIXIS: 400B, Acton, NJ). This spectrometer is connected to the side port of an epifluorescence microscope (Nikon TE-2000 U, Japan), which provides light selection (excitation: 470 ± 11 nm; dichroic: 484 nm long pass; emission: 496 nm long pass) and holds the sample cells. For sample preparation, the gold-coated microscope slides were first grafted with 1:1 Fc-C11SH/C12SH mixed SAMs, which were then subjected to an LSV (or a CV) scan either in a 1.0 mM aqueous solution of poly(fluorescein isothiocyanate allylamine hydrochloride) or in a 10 μ M aqueous solution of S'-fluorescein-labeled poly(adenine) 25-mer; potential scan rate: 100 mV/s. Following the electrochemical treatment, the SAMs were thoroughly rinsed with



Potential (V vs. Ag/AgCl)

Figure 1. Voltammetric monitoring of Fc SAMs undergoing either linear or cyclic potential sweeps in 1.0 mM poly(acrylic acid sodium salt) (PAA, MW 8000 Da) aqueous solutions. (a) Voltammetric monitoring of 1:1 Fc-C11SH/C12SH mixed SAMs treated by a cyclic potential sweep in 1.0 mM PAA. CVs shown in black were acquired in 0.1 M NaClO₄ aqueous solutions before (solid line) and after (dashed line) the CV scan in PAA. A control CV (in gray) obtained in 0.1 M NaCl is also included. (b) Voltammetric monitoring of 1:1 Fc-C11SH/C12SH mixed SAMs undergoing 10 consecutive cyclic potential scans in 1.0 mM PAA; the red arrows point to the direction of current decrease. (c) Voltammetric monitoring of 1:1 Fc-C11SH/C12SH mixed SAMs undergoing a linear potential sweep in 1.0 mM PAA. (d) Voltammetric monitoring of pure Fc-C11SH SAMs undergoing a linear potential scan rate: 100 mV/s.

deionized water to remove unbound polyelectrolytes. The resulting films remain immersed in deionized water during the entire course of fluorescence acquisition.

Atomic Force Microscopy (AFM). AFM characterization of polymer-modified SAMs was carried out using a Bruker MultiMode 8 atomic force microscope (Bruker, USA) in air and at room temperature. Silicon nitride probes (Model: ScanAsyst AIR, Bruker) used in these measurements have a force constant of 0.4 N/m, a resonant frequency of 70 kHz, and a nominal tip radius of 2 nm and are operated in Scanasyst Air mode with a scan rate of 1 Hz and a resolution of 512 \times 512 pixels. The substrates used are semitransparent gold-coated microscope slides, on which ferrocene SAMs were first formed as described above. For deposition of polyelectrolytes, these SAMs were then subjected to a linear potential sweep from 0.1 to 0.8 V vs Ag/AgCl at 100 mV/s in the following aqueous solutions: 1.0 mM poly(acrylic acid sodium salt), MW ~ 15 kDa, and poly(L-lysine hydrochloride), MW ~ 16 kDa, and 0.1 μ M DNA from calf thymus. Thus, treated SAMs were thoroughly rinsed with deionized water and then dried under N2 before AFM scanning. All AFM images presented in this work are original with no graphical touchup.

Layer-by-Layer Polyelectrolyte Deposition. Pure Fc-C11SH SAMs deposited with poly(acrylic acid sodium salt) were used as the starting surfaces to build layer-by-layer polyelectrolyte films. These Fc-C11SH SAMs were formed on semitransparent gold-coated microscope slides, on which poly(acrylic acid sodium salt) (PAA, MW ~ 15 kDa) was deposited by a linear potential sweep from 0.1 to 0.8 V vs Ag/

AgCl at a scan rate of 100 mV/s in a 1.0 mM aqueous solution of PAA. The resulting films were thoroughly rinsed with deionized water and then incubated in a 1.0 mM aqueous solution of poly(fluorescein isothiocyanate allylamine hydrochloride) for 15 min. Four additional rounds of 15 min incubation were given alternately in 1.0 mM PAA and poly(fluorescein isothiocyanate allylamine hydrochloride) so they reached a total of 10 layers at the end of the deposition. In each round, a UV–vis absorption spectrum of the resultant film was taken with a UV–visible spectrophotometer (Cary 50 Bio, Varian).

RESULTS AND DISCUSSION

Electrochemical Treatments and Characterization. We initially hypothesized the following "trigger-and-trade" (TnT) scheme to electrostatically deposit polyanions, M^+ Poly⁻, where M^+ refers to the counterions, onto ferrocene-containing SAMs:

$$Fc-SAM - e^- \rightarrow Fc^+-SAM$$
 (1)

$$Fc^+-SAM + M^+Poly^- \rightarrow Poly^-Fc^+-SAM + M^+$$
 (2)

To test this hypothesis, we first carried out cyclic voltammetry (CV) on 1:1 Fc-C11SH/C12SH mixed SAMs in poly(acrylic acid sodium salt) (PAA, MW 8000 Da) aqueous solutions. To diagnose the impact of such treatments on the SAMs, we also ran separate CV scans on the same SAMs in 0.1 M NaClO₄ before and after each given treatment. As expected, the initial scan

returns a symmetrical, bell-shaped voltammogram that is typical for electrode-bound ferrocenes probed in perchlorate (Figure 1a). Compared to this standard response, the CV scan in PAA obtained afterward displays moderately sluggish ferrocene oxidation with its peak lagging the former by about 30 mV (CV in red, Figure 1a). This result confirms that 1 mM PAA, i.e., polymer plus its associated Na⁺, can sustain ferrocene oxidation sufficiently and, in addition, reveals PAA's lower tendency to ion pair with ferrocenium (Fc⁺) as compared to perchlorate. By stabilizing the reaction product, such ion pairing effectively improves the kinetics of and lowers the driving force required for ferrocene oxidation.^{16,17} This effect is clearly shown by the significantly more sluggish oxidation profile obtained in Cl⁻, a poor ion-pairing agent¹⁸ to Fc^+ (CV in gray, Figure 1a). When this PAA/CV-treated Fc-SAM was rescanned in 0.1 M NaClO₄, a ~14% decrease in the amount of electron transfer was observed (CV in dashed line, Figure 1a). Two processes may potentially be responsible for this decrease: (1) ferrocene loss from the SAM and (2) the intended polymer deposition. In the first case, it is well documented that Fc SAMs probed in hydrophilic small ions such as Cl⁻ often suffer from electroactivity decays¹⁸⁻²⁰ upon extended potential bias, pointing to the susceptibility of ferrocenium (Fc⁺) to secondary reactions^{21,22} such as nucleophilic attacks when not properly protected, e.g., via ion pairing. To better gauge the contribution of this mechanism to the observed decay, we then examined fresh Fc-C11SH/C12SH mixed SAMs under more stringent conditions. Subjected to 10 consecutive CV scans in PAA, the SAM displays progressively decreasing ferrocene redox features, with the largest decrease occurring during the first scan (Figure 1b). Upon completion, this treatment registers a \sim 45% decrease in redox activity of the SAM when probed in 0.1 M NaClO₄, which is comparable to the level of decrease obtained from SAMs similarly treated in 0.1 M NaCl (data not shown). In comparison, no appreciable loss was observed from SAMs similarly treated in 0.1 M NaClO₄. These results thus point to the likely occurrence of ferrocene loss from the SAM when oxidized in polyanion aqueous solutions. To minimize such losses, therefore, it is preferable to subject these Fc SAMs only to a short period of potential bias.

On the other hand, PAA deposition may as well induce Fc activity decrease either by lowering the amount of Fc available for oxidation (due to Fc⁺PAA⁻ complexation) or by physically limiting perchlorate's access to the SAM surface (i.e., partial blocking) during the subsequent scan. Follow-up voltammetric measurements showed the first signs of this process. For example, when freshly prepared SAMs of the same composition were treated by a linear potential sweep (LSV) instead of CV in the presence of PAA, a larger decrease, $\sim 20\%$, was obtained (Figure 1c). This result argues against the material-loss mechanism—or, at least not as the sole mechanism in operation, because the Fc SAM was under longer potential bias in the CV treatment, which would have led to a greater loss and hence a larger decrease in electroactivity. Rather, this observation can be readily explained by the deposition scheme, in that the backward potential scan reduces most Fc⁺ back to Fc, which lifts the electrostatic attraction and in turn causes some deposited PAA to desorb from the SAM. This was found to be indeed the case, for example, from fluorescence spectroscopic characterization (next section).

Additional voltammetric runs were also carried out using Fc SAMs of different compositions and on other polyanions. For example, when pure Fc SAMs were employed instead of FcC11SH/C12SH mixed SAMs, an LSV treatment in PAA led to a \sim 24% decrease of the ferrocene redox response (Figure 1d), which is slightly larger than that obtained from the mixed Fc SAMs similarly treated. Provided that such a decrease is indeed indicative of polymer deposition, this result hints at the important possibility to control the amount of deposited polymer via Fc surface density in the SAM. On the other hand, we confirm the observation of similar trends when different polyanions or polyanions of different molecular weights were examined. One of such measurements, based on 7.5 kDa poly(L-glutamic acid, sodium salt) and mixed Fc SAMs, is presented in Supporting Information Figure 1.

Similar voltammetric treatments were also extended to cationic polymers, which, surprisingly, led to partial activity loss in Fc-SAMs as well. As shown in Figure 2a, this amounts to a



Figure 2. Voltammetric monitoring of 1:1 Fc-C11SH/C12SH mixed SAMs undergoing linear (a) and cyclic (b) potential sweeps in 1.0 mM poly(L-lysine hydrochloride) (PL, MW 8200 Da) aqueous solutions. All CVs shown in black were acquired in 0.1 M NaClO₄ aqueous solutions, whereas voltammograms shown in green and red were recorded in 1.0 mM PL dissolved in water. A control CV (in gray) obtained in 0.1 M NaCl is also included in (b). Potential scan rate: 100 mV/s.

16% decrease after the 1:1 Fc-C11SH/C12SH mixed SAM is treated by a single LSV scan in a poly(L-lysine hydrochloride) (PL, MW 8200 Da) aqueous solution. This result is unexpected, as it stands to suggest deposition of polymers carrying the same (positive) charge as the surface. Compared to the case of anionic PAA, the LSV response obtained here displays significantly more sluggish ferrocene oxidation, whose peak lags the one obtained in NaClO₄ by >200 mV. When we treat the mixed SAMs with a single CV scan instead, a smaller (~9%) decrease in ferrocene activity results (Figure 2b). Here, interestingly, the second CV in NaClO₄ consistently emerges a few tens of millivolts more positive than the first one. This shift is likely due to the deposited PLs, whose presence modifies the local charge environment around the Fc moieties and makes electron removal from the latter more costly. Potential shifts of similar nature have been previously observed, for example, on binary SAMs containing ferrocenes²³ as well as redox-active polyelectrolyte films.²⁴ Such a positive shift is also discernible from the LSV-treated SAMs but not as large, ~ 10 mV. In contrast, no shifts were found from the SAMs treated by either LSV or CV in the presence of PAA (Figure 1). This characteristic shift, therefore, once again suggests polycation deposition on Fc SAMs upon electrooxidation. Another polycation tested, poly(allylamine HCl), produces even more pronounced sluggishness and shifts when similarly treated (Supporting Informaton Figure 2). To gain a better understanding of the involved deposition processes, we thus moved onto other techniques for characterization of these films.

Fluorescence Spectroscopy. Shown in Figure 3 are fluorescence emission spectra acquired directly on 1:1 Fc-C11SH/C12SH mixed SAM surfaces that have undergone various treatments with polyelectrolytes. The fluorophore probed here is fluorescein, which appears in the tested polycation in the form of poly(fluorescein isothiocyanate allylamine hydrochloride) and the polyanion, 5'-labeled adenine 25-mer. Due to existence of multiple complicating factors, such as fluorescence quenching (by gold²⁵ as well as ferrocene²⁶) and variations in polymer conformation and placement, we focus here on identifying the trend in the signals. As evident from Figure 3a, both single LSV and CV treatments lead to successful polycation deposition, with the former displaying slightly but consistently higher fluorescence intensity. By contrast, very little deposition resulted from the following controls: (1) 30 min incubation of the SAM in the polymer solution (i.e., no electrochemical treatment) or (2) a single LSV scan of pure C12 SAM in polymer (i.e., no ferrocene). These negative controls thus confirm the necessity of electrochemically modifying the surface charge of these SAMs in order to achieve polymer deposition. A similar trend is also observed in the case of polyanions (Figure 3b). In accordance with the voltammetric evidence presented earlier, these results show a very minor polymer desorption upon the returning potential scan. Such irreversibility is generally observed in electrostatic polyelectrolyte deposition and points to the existence of other intermolecular forces, such as van der Waals and hydrophobic interactions, besides electrostatic attraction, in facilitating polymer surface binding.

Water Contact Angle Measurements. Water contact angles measurements were also conducted on these Fccontaining SAMs subjected to similar electrochemical treatments (Table 2 and Supporting Information Figure 3). As expected, the untreated 1:1 Fc-C11SH/C12SH mixed SAM displays a relatively hydrophobic surface with a water contact angle of about 91°, which decreases only slightly after the SAM undergoes an LSV scan in water alone, 88°. By contrast, the SAM similarly treated in PAA gives a water contact angle of about 71°, indicating a more hydrophilic surface as a result of PAA deposition. If the SAM is treated by 10 consecutive CV scans instead, a very comparable angle, 72°, results, suggesting that deposition occurs mostly during the initial scan. On pure Fc SAMs, a lower angle, ~64°, is observed upon the same LSV



Figure 3. Fluorescence spectroscopic characterization of electrochemically triggered polyelectrolyte deposition processes. (a) Representative fluorescence emission spectra collected on 1:1 Fc-C11SH/C12SH mixed SAMs or pure C12SH SAMs undergoing various treatments. All treatments were carried out in 1.0 mM poly(fluorescein isothiocyanate allylamine hydrochloride) (MW 16 200 Da) aqueous solutions. (b) Representative fluorescence emission spectra collected on 1:1 Fc-C11SH/C12SH mixed SAMs undergoing either CV deposition (green) or 30 min incubation (black) in 50.0 μ M 5'-fluorescein-labeled adenine 25-mer (MW ~ 8300 Da). The embedded cartoons depict the charge and skeleton of the fluorescent polyelectrolytes employed.

Table 2. Water Contact Angle (in Degree) Measurements^a

polymer	1:1 mixed Fc-C11SH/ C12SH	100% Fc- C11SH
SAM alone	90.7 ± 0.4^{b}	82.8 ± 0.5^{b}
	$88.1 \pm 0.5^{\circ}$	
poly(acrylic acid sodium salt)	71.4 ± 0.6^{c}	63.5 ± 1.5^{c}
	72.1 ± 6.4^{d}	
poly(L-lysine HCl)	87.3 ± 0.2^{c}	$81.7 \pm 3.6^{\circ}$
poly(allylamine HCl)	$82.6 \pm 4.3^{\circ}$	$86.9 \pm 1.7^{\circ}$

^{*a*}Images from which these water contact angles are measured are presented in Supporting Information Figure 3. All SAMs are treated by an LSV scan unless otherwise specified. ^{*b*}Fresh SAM with no treatment. ^{*c*}LSV from 0.1 to 0.8 V vs Ag/AgCl in water. ^{*d*}Ten consecutive CVs from 0.1 to 0.8 V in water; standard deviation values are based on at least three parallel measurements obtained from either one or two samples.

treatment, which is suggestive of a higher PAA surface coverage due to higher Fc density. In marked contrast, SAMs similarly treated in the presence of polycations only yield negligible (in the case of polylysine) to minor (in the case of polyallylamine) changes in water contact angles. These results thus point to the distinctive surface characteristics between deposited polyanions and polycations, which in turn suggest different deposition mechanisms involved.

Electrochemical Quartz Crystal Microbalance (EQCM). We next followed the deposition of PAA and PL, each in three molecular weights, using electrochemical quartz crystal microbalance. For the anionic PAA of 8 and 15 kDa, the crystal oscillation frequencies start to drop almost immediately after the potential sweep commences (dotted and dashed traces in green, Figure 4), indicating mass gain at the SAM surface as a result of



Figure 4. Electrochemical QCM monitoring of polyelectrolyte deposition on 1:1 Fc-C11SH/C12SH mixed SAMs. Responses of crystal oscillation frequency shift vs time obtained from 1.0 mM PAA (anionic) and PL (cationic) in water are shown in green and red, respectively. In each case, the solution-facing gold electrode on the crystal is biased between 0.1 and 0.8 V vs Ag/AgCl with a scan rate of 100 mV/s (waveform shown in solid black). A control response (in blue) recorded in water only is also included. The first complete CV scan is highlighted by light yellow/blue stripes.

polymer deposition. In both cases, the drop is quickly replaced by a new frequency rise that reaches a local maximum at around 0.3 V vs Ag/AgCl, thereby registering a frequency decrease of 4 Hz (8 kDa) and 5 Hz (15 kDa), respectively. Past the maximum, the frequency drops back down slowly toward the end of the forward potential scan at 0.8 V. Immediately following the start of the backward scan, a much larger frequency drop kicks in, producing a frequency decrease of 27 Hz (8 kDa) and 25 Hz (15 kDa) at the completion of the backward scan (regions highlighted in light blue, Figure 4). On subsequent CV scans, the frequency profiles track the applied potential closely, but not exactly. On a closer look, it can be discerned that the frequency maxima/minima consistently precede the potential maxima/ minima (0.8 and 0.1 V, respectively). These frequency maxima/ minima are not constant from scan to scan, moreover. As the potential scan proceeds, the maxima decrease progressively, while the minima increase, thus narrowing the frequency swing in between. This tendency is more pronounced in the case of 15 kDa PAA, measuring 11 vs 18 Hz for the 8 kDa PAA, at the end of the final CV scan. In both cases, a stable baseline follows the

potential switch-off. In comparison to these two cases, the 2.1 kDa PAA similarly probed displays much smaller frequency shifts as well as a different shift profile (solid trace in green, Figure 4). Starting off, the crystal oscillation frequency shifts downward only slightly, which is then superseded by a similar but more powerful frequency increase that produces a local maximum at around 0.25 V. From that point on, the frequency continues to drop until the forward scan completes, which, upon potential reversal, starts to rise again. This produces a new frequency maximum, beyond which the frequency drops sharply and reaches a minimum at the end of the backward scan. Consecutive CV scans afterward produce a profile that generally resembles the other two cases, except that each frequency maximum now contains edges and between them a local minimum. On the other hand, control measurements conducted in water alone only yield a low-magnitude, despite potentialresponding, profile, which reestablishes the initial frequency baseline at the end of each forward scan as well as at the completion of the consecutive CV treatment (solid trace in blue, Figure 4).

Similar EQCM characterization of cationic PLs deposition reveals a number of distinctive features as compared to PAAs (traces in red, Figure 4). (1) During the initial potential scan: For PLs of 3.3 and 8.2 kDa, the first forward scan lead to a monotonous frequency downshift starting at ~0.3 V. The 16 kDa PL behaves quite differently, in that the frequency initially drops slightly and then rises abruptly at 0.4 V. (2) Subsequent potential cycles: Here, once again, PLs of 3.3 and 8.2 kDa share the same trend, in which the frequency increases/decreases are brought forth by the backward/forward potential scans, respectively; matching frequency/potential highs and lows are instead observed from the 16 kDa PL. (3) Extent of frequency fluctuation: In all three cases, the magnitude of frequency shifts becomes relatively stable after the first potential cycle. (4) Net frequency shifts: For all three PLs, a positive frequency shift in the range of 4-6 Hz results at the completion of the potential cycle. By contrast, all PAAs produce negative net frequency shifts: -9 Hz for the 2.1 kDa and about -28 Hz for the other two. (5) The smallest PL (3.3 kDa) displays relatively flat frequency maxima as opposed to peaks from the other two in the series, which in a way is consistent with the PAA series.

EQCM provides highly convoluted information about the deposition processes because the deposited polymers simultaneously change the surface mass, viscoelasticity, and SAM/water interfacial slippage condition, each modifying the crystal oscillation frequency in its own fashion.²⁷ Complicating the matter further are secondary processes caused by the applied potential bias, such as the swelling/shrinking of deposited polymers and accompanying ingress/egress of counterions and water. Fortunately, these secondary processes cannot take effect prior to polymer deposition. This thus points to the initial potential scan as the only window to observe the deposition alone, where the correspondence between frequency drops and polymer deposition suggests itself (yellow-highlighted region, Figure 4). Once deposited, both polyanions and polycations will electrostatically respond to the applied potential, which continues to drive the Fc/Fc⁺ redox cycles. In the case of PAA, the reduction of Fc⁺ back to Fc on the returning scan (blue-highlighted region, Figure 4) lifts the electrostatic attraction between Fc⁺ and PAA, producing a mechanically more relaxed and elastic structure. An influx of sodium ions, accompanied by their water shells, is also expected, so that the newly liberated negative charges on PAA can be neutralized.

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Collectively, these structural/compositional/mechanical changes register a large and abrupt frequency decrease on the oscillating crystal. The next forward potential sweep reverses the processes, whereupon a more adherent and rigid PAA layer enables the crystal to oscillate at a higher frequency. As the potential cycle continues, these processes repeat accordingly. Similar potential-modulated QCM responses have been observed previously, for example, from ferricyanide-doped polyelectrolyte films.¹⁴ Evaluating these PAA profiles together, we may reach two additional conclusions. First, the polyanion deposition is largely an irreversible process. This is evident from the similarity in QCM responses between the initial and subsequent scans, both operating on the same population of polymers deposited in the first scan. Such irreversibility is commonly found in LbL polyelectrolyte deposition²⁸ and can be generally attributed to (1) the large energy penalty associated with dissociating/rehydrating the surface and polymers, (2) the vanishingly small translational entropy²⁹ of polymers as compared to small solutes, and (3) the presence of other binding mechanisms, such as van der Waals interactions. Second, beyond the initial scan, the applied potential acts to "anneal" the deposited polyanions, as manifested by the progressively decreasing magnitude of frequency shifts. Such annealing effect is most visible in the 15 kDa PAA, whose long polymer chain affords the highest number of loose segments that are mostly responsive to the electric field among the three. The other interpretation of the observed trend would be a gradual loss of PAA deposits from the surface, which is considered less likely because of its absence from the case of 2.1 kDa PAA. With its short chain carrying the same charge density, such loss would have been at least comparable to the other two PAAs, if not more

On the polycation side, PL deposition on Fc SAMs can be unequivocally identified from their highly characteristic QCM profiles. Similar to PAAs, their deposition is electrochemically triggered and takes place during the initial scan. But unlike their anionic counterparts, which are electrostatically drawn to the oxidized Fc SAM, these polycations experience repulsion as they move toward and subsequently land on the similarly charged surface. To overcome this repulsion, therefore, their counterions, Cl⁻, have to be directly involved. A detailed discussion on this mechanism will be presented in a separate section below. As the potential shifts toward more negative (reducing) values on the returning scan, the deposited PLs are pulled further in, which leads to an overall more compact structure and hence the observed frequency upshift. The next forward potential scan sets everything on reverse: a relaxed film displaying a frequency downshift. As the potential scan continues, such shrinkage/ expansion processes take turns to dominate the resulting frequency response. These features are shared by the 3.3 and 8.2 kDa PLs, with their frequency maxima/minima completely "out of phase" with the applied potential. Between these two, the 3.3 kDa PL clearly responds to the applied potential faster than the other, likely due to its smaller size. In comparison, the frequency shift observed in the 16 kDa PL not only kicks in early but also is in phase with the applied potential. The latter feature, which notably resembles PAA's frequency profiles past the initial potential cycle, is not well understood at this moment.

Atomic Force Microscopy (AFM). To gain detailed information on the morphology of thus deposited polyelectrolytes, we also carried out AFM measurements. For the 15 kDa PAA LSV-deposited on the Fc mixed SAM, the resultant image appears largely featureless (Figure 5a). Since 15 kDa PAA is too



Figure 5. AFM characterization of polyelectrolyte deposition on Fc SAMs triggered by a linear potential sweep from 0.1 to 0.8 V vs Ag/AgCl. (a) 1.0 mM PAA (MW 15 000 Da) on a 1:1 Fc-C11SH/C12SH mixed SAM. (b) DNA from calf thymus (MW ~ 10–15 × 10⁶ Da) on a 1:1 Fc-C11SH/C12SH mixed SAM. (c) DNA from calf thymus on a pure Fc-C11SH SAM. (d) Height vs distance profiles of selected sections in images (a)–(c). Scan size: 2 × 2 μ m. See the Experimental Section for details.

small to be individually resolved with our current AFM setup, we cannot conclude from this image whether or not polyanion deposition has occurred. Similar results were also obtained from the 16 kDa PL as well as control samples run in water alone (Supporting Information Figure 4). To circumvent this limitation, we then replaced PAA with DNA from calf thymus, a much larger polyanion with a MW of 10–15 MDa. This time, AFM imaging clearly identifies twisted, threadlike features spanning several hundred nanometers (Figure 5b), which can be attributed to deposited DNAs with reasonable certainty. From their large sizes, i.e., tens of nanometers in width and >10 nm maximal height, we can further conclude that these threads represent bundles of DNA strands, whose formation may result from DNA minimizing hydrophobic contact. Beneath these DNA bundles, interestingly, another meshlike feature is also clearly visible. These meshes are relatively evenly distributed across the entire surface, and their sizes fall within a narrow range of 15-20 nm. Since this formation is exclusively observed for DNA, i.e., absent from SAMs similarly treated in PAA, PL, or water alone, we tentatively assign it to be the second main feature of DNA deposition besides the threads. To further verify this assignment, we also imaged DNA deposits formed on pure Fc SAMs, which, once again, display a meshlike morphology (Figure 5c). Here, a noticeable difference is that the DNAs deposited atop appear not only thinner but also shorter, which appear to resemble individual DNAs more than their bundles. This morphological difference may be due to the fact that, absent of hydrophobic C12 thiols, pure Fc SAMs produce a primarily charged surface upon oxidization, which can better accommodate binding of individual DNAs. By contrast, oxidation of the Fc-C11SH/C12SH mixed SAM yields a partially charged surface blended with hydrophobic components. From these images, we can further conclude that such



Figure 6. Schematic illustration of mechanisms involved in the electrochemically triggered deposition of polyelectrolytes. Polyanions and polycations are depicted by thick curves in blue and yellow, respectively, whereas their counterions are presented by small dots (gray for cations and green for anions). Intrinsic charges on polyelectrolytes are shown by circles.

electrochemically triggered polymer deposition proceeds evenly across the entire SAM surface.

Deposition Mechanisms. All the experimental evidence presented above suggests that the "trigger-and-trade" scheme describes the polyanion deposition reasonably well. Among these, the results of fluorescence, contact angles, and AFM uniformly confirm the occurrence of such deposition, whereas the CV and EQCM data further shed light on the involved mechanism and dynamics. Of the latter, the well-defined Fc oxidation waves obtained in PAA (Figure 1) and poly(glutamic acid, sodium salt) (Supporting Information Figure 1) manifest their direct involvement and efficacy in charge compensation, despite their relatively low concentration and large size (e.g., vs 0.1 M NaCl). The EQCM responses of PAA (Figure 4) during the initial potential scan, on the other hand, identify a trend in which the mass gain on the electrode closely tracks the Fc oxidation. These results help establish a general sequence of events involved in the deposition: ferrocene oxidation \rightarrow charge compensation \rightarrow polyanion deposition (Figure 6). Though not directly related, it should be pointed out that a similar scheme has been conceived by Badia and co-workers to attract anionic surfactants onto Fc SAMs.³⁰

The characteristically distinctive responses observed in polycations signify a different deposition mechanism all together. This becomes evident first from voltammetry, in which Fc oxidation in the presence of polycations is found to significantly lag behind that obtained in polyanion solutions. Of these, the CV obtained in PL closely resembles that in NaCl

(Figure 2b), suggesting that chloride, the common anion of the two electrolytes, is responsible for compensating Fc⁺. Nevertheless, these two voltammograms are not exactly identical: Fc oxidation in NaCl not only appears slightly more dragged out but also peaks earlier than the other. The latter shift is not caused by conductivity difference between the two solutions (i.e., the *iR* drop), which remains observable in 1 mM as well as 1.0 M NaCl solutions (data not shown). A similar but even more pronounced trend was found in the case of poly(allylamine HCl) (Supporting Information Figure 2). These distinctive features thus lead us to an important conclusion: the movement of small counterions in polyelectrolyte aqueous solutions is not completely independent of the polymer. For this to be true, therefore, a certain level of association must exist between polyelectrolytes and their counterions when dispersed in water. Understandably, the strength and extent of such association is polymer dependent. In the case of PL, the pendant positive charge is located on the ε -position distant from the polymer backbone, which gives rise to a relatively "delocalized" charge distribution along the polymer. This in effect lowers the density of intrinsic charge carried by the polyanion and thus undermines its ability to electrostatically attract its counterion, Cl⁻. As a result, a significant portion of chloride ions in the system can move about nearly as freely as in NaCl. By contrast, charges are more locally distributed along the polymer in the case of poly(allylamine HCl), thanks to the close placement of its ammonium group to the polymer backbone. This results in a higher level of association between polymers and their

counterions at any given time, due to stronger electrostatic attraction and an elevated need to screen the monomermonomer charge repulsion within the polymer. Consequently, to call these polymer-associated counterions to participate in charge compensation, a higher energy input is required, as manifested by its positive-shifted Fc oxidation potential (Supporting Information Figure 2). Once these chloride ions start to move toward the electrode, critically, they drag the associated polymers along with them. To see the feasibility of this potential-induced co-movement, we may first invoke an analogy with another electrokinetic phenomenon-electroosmosis (EO). In the latter process, counterions accumulated in the double layer of a charged surface can carry water molecules to produce bulk solution movement under an external electric field.³¹ With their stronger (charge-charge vs chargedipole interaction in EO) and multiple binding with Cl-, polycations in the current case are expected to be even more susceptible to such induced motion. Accepting this possibility for the time being, we immediately arrive at another important conclusion: electrochemically triggered polycation deposition involves like-charge attraction. This has to be true because the polymer plus associated counterions are net positively charged-the same as the oxidized Fc SAM.

Additional insights emerge when these electrochemically triggered processes are evaluated in light of established polyelectrolyte theories. In the classical Oosawa–Manning (OM) ion condensation theory,^{32–34} small counterions are postulated to distribute between two states in aqueous polyelectrolyte solutions: freely mobile vs territorially bound with polymers. Underlying this distribution is the thermodynamic balance between electrostatic attraction, which pulls the counterions within close proximity to the polymer, and the entropic gain associated with the release of counterions into the bulk. A key parameter formulated in the OM theory is Manning linear charge density of the polyelectrolyte, ξ , which can be calculated from the following equation: $\xi = e^2 / \varepsilon k_B T b$, where *e* is the elementary charge, ε the dielectric constant of the solvent, $k_{\rm B}T$ the thermal energy term, and b the average axial charge spacing of the polymer. Theoretically, counterion condensation sets in whenever ξ becomes greater than 1.^{33,34} From this dimensionless quantity, one can also estimate the fraction of condensed ions, *f*, which takes the value of $1 - (Z\xi)^{-1}$, where Z is the valence charge of the counterion. Approximating b to be 0.3 nm for poly(allylamine HCl),³⁵ we thus obtain $\xi = 2.3$ and f =0.6 (in water and at 25 °C), which suggest substantial ion condensation. In comparison, such condensation is considerably less in the case of PL due to its larger charge spacing, e.g., in the range of 0.5–0.7 nm, depending on its secondary structure.³⁶ These numerical estimates thus corroborate well with our qualitative analysis above.

An important implication of ion condensation theory is attraction between polyelectrolytes carrying similar charges. This counterintuitive phenomenon arises because (1) the polyelectrolyte plus its counterions is a highly polarizable entity; as such, (2) thermal fluctuation causes temporary, but constant, uneven charge distribution along the polymer; and (3) correlated polarization between polyelectrolytes in close proximity lowers the total energy of the system. The latter, as Oosawa put forth first in his celebrated monograph, *Polyelectrolytes*, "…results in an attractive force between macroions, just as in the case of van der Waals interaction between atoms and molecules".³² This thus leads to a peculiar scenario in which mobile ion clouds are shared by interacting polymers.³⁷

While this phenomenon is prevalent and relatively well understood in cases where polyvalent counterions are directly involved, e.g., in DNA/dication binding,^{38,39} recent theoretical and experimental evidence^{37,40} strongly suggests that like-charge attraction can be also mediated by monovalent ions. Besides polyelectrolytes, similar theoretical treatments⁴¹ can also be extended to explain attraction between like-charged surfaces. In this regard, therefore, our results on polycation deposition provide experimental evidence that the hybrid scenario, i.e., attraction between similarly charged polyelectrolytes and surfaces, also occurs (Figure 6).

Still, such attraction would not proceed without the electrochemical trigger. Electrooxidation not only puts charge on the Fc-SAM surface but, in doing so, also provides the driving force for polyelectrolytes (i.e., polymers plus counterions) to migrate toward the surface. In between the two binding parties, importantly, the applied potential also tips the thermodynamic and mechanical balances at the Fc-SAM/water interface. Prior to oxidation, both mixed and pure Fc SAMs are moderately hydrophobic (Table 2). To cope with such hydrophobicity and at the same time maximally maintain their H-bonding network, water molecules in direct contact with the surface collectively will have to adopt a certain nonrandom orientation. As oxidation brings charges onto the hydrophobic SAM, many interfacial water molecules find themselves in wrong orientations so a major restructuring is due. Similar processes can also be expected of the incoming polyelectrolytes. In the case of polyanions, these may involve shedding of counterions and reorganization of polymer segments, presumably guided by the local surface charge distribution, so that Fc⁺ moieties can be neutralized fully and effectively. Such restructuring should be less for polycations because their binding to Fc⁺ is led by small counterions (no shedding is necessary, therefore), whose nimble movement allows quick adjustment of charge distribution around the polymers. This important distinction between polyanions and polycations is expected to cause further divergences after their landing, i.e., conformation/packing of deposited polyelectrolytes as well as the associated interfacial water structure. Such microscopic characteristics, in turn, lead to experimentally observable differences, e.g., the constantly smaller signal fluctuations and deviations in EQCM (Figure 4) and water contact angles (Table 2) obtained from polycations.

While the mechanisms discussed above are clearly plausible, it must be stressed that other parameters and scenarios, either operating alone or alongside electrostatic interactions, may also exist. For example, we have not explicitly considered the influence of lateral surface heterogeneity, which can be particularly relevant in the case of mixed Fc SAMs. In the case of polycations, moreover, deposition may as well result from their decreased solubility as the Cl⁻ exodus (upon Fc oxidation) causes the deprotonation, and hence neutralization, of these polymers. All these potential contributors attest the complexity of involved processes, which we hope to continue to explore in the near future.

Layer-by-Layer Deposition. Finally, as a preliminary effort to explore the potential applications of this deposition strategy, we examined the formation of conventional layer-by-layer (LbL) polyelectrolyte films starting with an electrochemically deposited first polyelectrolyte layer. This, if successful, should promise a general formation strategy for electroactive LbL films, whose ferrocene adlayer can be exploited for both diagnosis and electroactuation purposes. As shown in Figure 7, PAA films LSV-deposited on pure Fc-C11SH SAMs can indeed serve as the



Figure 7. Layer-by-layer polyelectrolyte deposition starting from a PAA layer deposited by the reported method. (a) Ten-layer film growth monitored by UV-vis absorption responses of poly(fluorescein isothiocyanate allylamine hydrochloride), which is deposited at evennumbered rounds. (b) Net UV-vis absorbance of poly(fluorescein isothiocyanate allylamine hydrochloride) monitored at ~505 nm vs number of layers, replotted from (a).

starting surface to sustain the growth of LbL polyelectrolyte films. For the 10-layer PAA/poly(fluorescein isothiocyanate allylamine) films investigated here, moreover, we observed a nonlinear layer-by-layer growth profile. More detailed studies along this direction are currently ongoing in our laboratory to establish the structure and general properties of these electroactive polyelectrolyte films.

SUMMARY AND OUTLOOK

Above we have presented a new approach to polyelectrolyte surface deposition based on electrochemical triggering. Starting from the same basic structure, ferrocene-decorated selfassembled monolayers (Fc-SAMs), this approach enables quantitative deposition of both polyanions and polycations with a wide range of chemical identities (synthetic polymers, peptides, and DNA) and molecular weights $(10^3 - 10^7 \text{ Da})$. Such generality, combined with its ready access to conventional layerby-layer film formation and electrochemical detection, should make this approach useful in a number of areas, for example, in polyelectrolyte-based diagnosis and electroactuation. Conceivably, the methodology detailed here may also be of some value in probing aqueous polyelectrolyte systems, in particular, their organization and mass transfer. To this end, for example, Osteryoung and co-workers demonstrated previously that quantitative information about counterion diffusion (in polyelectrolyte solutions⁴² and their colloidal suspensions⁴³) could be extracted from steady-state voltammetry of proton

reduction on microelectrodes. Compared to their approach, our Fc-SAM-based methodology imposes little restriction on experimental conditions under which the polyelectrolytes can be examined, such as pH or the type of ions. As such, it enables counterions in polyelectrolytes to be directly compared to their simple ion counterparts. While a fair amount of information can already be obtained from Fc/Fc^+ voltammetry alone, such as shape, shift, and onset, additional information is possible when it is further coupled with a secondary technique, e.g., QCM. Some of these possibilities are currently being tested in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.8b02671.

Cyclic voltammetric characterization of deposition of additional polyanions/polycations; photographs of water droplets obtained in water contact angle analysis; additional AFM images of 1:1 Fc-C11SH/C12SH mixed SAMs treated in polylysine and water (PDF)

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Notes

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REFERENCES

(1) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1169.

(2) Chidsey, C. E. D. Free Energy and Temperature Dependence of Electron Transfer at the Metal-Electrolyte Interface. *Science* **1991**, *251*, 919–922.

(3) Smalley, J. F.; Finklea, H. O.; Chidsey, C. E. D.; Linford, M. R.; Creager, S. E.; Ferraris, J. P.; Chalfant, K.; Zawodzinsk, T.; Feldberg, S. W.; Newton, M. D. Heterogeneous Electron-Transfer Kinetics for Ruthenium and Ferrocene Redox Moieties through Alkanethiol Monolayers on Gold. J. Am. Chem. Soc. **2003**, 125, 2004–2013.

(4) Eckermann, A. L.; Feld, D. J.; Shaw, J. A.; Meade, T. J. Electrochemistry of Redox-active Self-Assembled Monolayers. *Coord. Chem. Rev.* **2010**, *254*, 1769–1802.

(5) Umek, R. M.; Lin, S. W.; Vielmetter, J.; Terbrueggen, R. H.; Irvine, B.; Yu, C. J.; Kayyem, J. F.; Yowanto, H.; Blackburn, G. F.; Farkas, D. H.; Chen, Y.-P. Electronic Detection of Nucleic Acids – *A Versatile Platform for Molecular Diagnostics. J. Mol. Diagn.* **2001**, *3*, 74–84.

(6) Fan, C.; Plaxco, K. W.; Heeger, A. J. Electrochemical Interrogation of Conformational Changes as a Reagentless Method for the Sequence-Specific Detection of DNA. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 9134–9137.

(7) Norman, L. L.; Badia, A. Redox Actuation of a Microcantilever Driven by a Self-Assembled Ferrocenylundecanethiolate Monolayer: An Investigation of the Origin of the Micromechanical Motion and Surface Stress. J. Am. Chem. Soc. **2009**, 131, 2328–2337. (8) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. Vectorial Multistep Electron Transfer at the Gold Electrodes Modified with Self-Assembled Monolayers of Ferrocene-Porphyrin-Fullerene Triads. *J. Phys. Chem. B* **2000**, *104*, 2099–2108.

(9) Xie, H.; Jiang, K.; Zhan, W. A Modular Molecular Photovoltaic System Based on Phospholipid/Alkanethiol Hybrid Bilayers: Photocurrent Generation and Modulation. *Phys. Chem. Chem. Phys.* **2011**, *13*, 17712–17721.

(10) Clark, S. L.; Montague, M.; Hammond, P. T. Selective Deposition in Multilayer Assembly: SAMs as Molecular Templates. *Supramol. Sci.* **1997**, *4*, 141–146.

(11) Harris, J. J.; Bruening, M. L. Electrochemical and in Situ Ellipsometric Investigation of the Permeability and Stability of Layered Polyelectrolyte Films. *Langmuir* **2000**, *16*, 2006–2013.

(12) Hodak, J.; Etchenique, R.; Calvo, E. J.; Singhal, K.; Bartlett, P. N. Layer-by-Layer Self-Assembly of Glucose Oxidase with a Poly-(allylamine)ferrocene Redox Mediator. *Langmuir* **1997**, *13*, 2708–2716.

(13) Lvov, Y. M.; Lu, Z.; Schenkman, J. B.; Zu, X.; Rusling, J. F. Direct Electrochemistry of Myoglobin and Cytochrome $P450_{cam}$ in Alternate Layer-by-Layer Films with DNA and Other Polyions. *J. Am. Chem. Soc.* **1998**, *120*, 4073–4080.

(14) Grieshaber, D.; Vörös, J.; Zambelli, T.; Ball, V.; Schaaf, P.; Voegel, J.-C.; Boulmedais, F. Swelling and Contraction of Ferrocyanide-Containing Polyelectrolyte Multilayers upon Application of an Electric Potential. *Langmuir* **2008**, *24*, 13668–13676.

(15) Schmidt, D. J.; Cebeci, F. Ç.; Kalcioglu, Z. I.; Wyman, S. G.; Ortiz, C.; Van Vliet, K. J.; Hammond, P. T. Electrochemically Controlled Swelling and Mechanical Properties of a Polymer Nanocomposite. *ACS Nano* **2009**, *3*, 2207–2216.

(16) Rowe, G. K.; Creager, S. E. Redox and Ion-Pairing Thermodynamics in Self-Assembled Monolayers. *Langmuir* **1991**, *7*, 2307–2312.

(17) Ju, H.; Leech, D. Effect of Electrolytes on the Electrochemical Behavior of 11-(Ferrocenylcarbonyloxy)undecanethiol SAMs on Gold Disk Electrodes. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1549–1554.

(18) Valincius, G.; Niaura, G.; Kazakevičienė, B.; Talaikytė, Z.; Kažemėkaitė, M.; Butkus, E.; Razumas, V. Anion Effect on Mediated Electron Transfer through Ferrocene-Terminated Self-Assembled Monolayers. *Langmuir* **2004**, *20*, 6631–6638.

(19) Popenoe, D. D.; Deinhammer, R. S.; Porter, M. D. Infrared Spectroelectrochemical Characterization of Ferrocene-Terminated Alkanethiolate Monolayers at Gold. *Langmuir* **1992**, *8*, 2521–2530.

(20) Abbott, N. L.; Whitesides, G. M. Potential-Dependent Wetting of Aqueous Solutions on Self-Assembled Monolayers Formed from 15-(Ferrocenylcarbonyl)pentadecanethiol on Gold. *Langmuir* **1994**, *10*, 1493–1497.

(21) Jego-Evanno, P.; Hurvois, J. P.; Moinet, C. Electrooxidation of Substituted Ferrocenes: Indirect Oxidation of the Side Chain. *J. Electroanal. Chem.* **2001**, *507*, 270–274.

(22) Hurvois, J. P.; Moinet, C. Reactivity of Ferrocenium Cations with Molecular Oxygen in Polar Organic Solvents: Decomposition, Redox reactions and Stabilization. J. Organomet. Chem. **2005**, 690, 1829–1839.

(23) Lee, L. Y. S.; Sutherland, T. C.; Rucareanu, S.; Lennox, R. B. Ferrocenylalkylthiolates as a Probe of Heterogeneity in Binary Self-Assembled Monolayers on Gold. *Langmuir* **2006**, *22*, 4438–4444.

(24) Tagliazucchi, M.; Calvo, E. J.; Szleifer, I. A Molecular Theory of Chemically Modified Electrodes with Self-Assembled Redox Polyelectrolye Thin Films: Reversible Cyclic Voltammetry. *Electrochim. Acta* **2008**, *53*, 6740–6752.

(25) Kittredge, K. W.; Fox, M. A.; Whitesell, J. K. Effect of Alkyl Chain Length on the Fluorescence of 9-Alkylfluorenyl Thiols as Self-Assembled Monolayers on Gold. *J. Phys. Chem. B* **2001**, *105*, 10594–10599.

(26) Fery-Forgues, S.; Delavaux-Nicot, B. Ferrocene and Ferrocenyl Derivatives in Luminescent Systems. *J. Photochem. Photobiol., A* **2000**, 132, 137–159.

(27) Buttry, D. A.; Ward, M. D. Measurement of Interfacial Processes at Electrode Surfaces with the Electrochemical Quartz Crystal Microbalance. *Chem. Rev.* **1992**, *92*, 1355–1379.

(28) Dubas, S. T.; Schlenoff, J. B. Factors Controlling the Growth of Polyelectrolyte Multilayers. *Macromolecules* **1999**, *32*, 8153–8160.

(29) Netz, R. R.; Andelman, D. Neutral and Charged Polymers at Interfaces. *Phys. Rep.* 2003, 380, 1–95.

(30) Nguyen, K.-L.; Dionne, E. R.; Badia, A. Redox-Controlled Ion-Pairing Association of Anionic Surfactant to Ferrocene-Terminated Self-Assembled Monolayers. *Langmuir* **2015**, *31*, 6385–6394.

(31) Evans, D. F.; Wennerström, H. *The Colloidal Domain*; Wiley-VCH: New York, 1999.

(32) Oosawa, F. *Polyelectrolytes*; Marcel Dekker, Inc.: New York, 1971.
(33) Manning, G. S. Counterion Binding in Polyelectrolyte Theory. *Acc. Chem. Res.* 1979, *12*, 443–449.

(34) Manning, G. S.; Ray, J. Fluctuations of Counterions Condensed on Charged Polymers. *Langmuir* **1994**, *10*, 962–966.

(35) Donath, E.; Walther, D.; Shilov, V. N.; Knippel, E.; Budde, A.; Lowack, K.; Helm, C. A.; Möhwald, H. Nonlinear Hairy Layer Theory of Electrophoretic Fingerprinting Applied to Consecutive Layer by Layer Polyelectrolyte Adsorption onto Charged Polystyrene Latex Particles. *Langmuir* **1997**, *13*, 5294–5305.

(36) Dos, A.; Schimming, V.; Tosoni, S.; Limbach, H.-H. Acid-Base Interactions and Secondary Structures of Poly-L-Lysine Probed by ¹⁵N and ¹³C Solid State NMR and *Ab initio* Model Calculations. *J. Phys. Chem. B* **2008**, *112*, 15604–15615.

(37) Naji, A.; Jungblut, S.; Moreira, A. G.; Netz, R. R. Electrostatic Interactions in Strongly Coupled Soft Matter. *Phys. A* **2005**, *352*, 131– 170.

(38) Gelbart, W. M.; Bruinsma, R. F.; Pincus, P. A.; Parsegian, V. A. DNA-Inspired Electrostatics. *Phys. Today* **2000**, *53*, 38–44.

(39) Diehl, A.; Carmona, H. A.; Levin, Y. Counterion Correlations and Attraction between Like-Charged Macromolecules. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2001**, *64*, 011804.

(40) Manning, G. S. Counterion Condensation Theory of Attraction Between Like Charges in the Absence of Multivalent Counterions. *Eur. Phys. J. E* **2011**, *34*, 132.

(41) Guldbrand, L.; Jönsson, B.; Wennerström, H.; Linse, P. Electrical Double Layer Forces. A Monte Carlo Study. *J. Chem. Phys.* **1984**, *80*, 2221–2228.

(42) Ciszkowska, M.; Osteryoung, J. G. Voltammetric Studies of Counterion Transport in Polyelectrolyte Solutions. *J. Phys. Chem.* **1994**, 98, 3194–3201.

(43) Roberts, J. M.; Linse, P.; Osteryoung, J. G. Voltammetric Studies of Counterion Diffusion in the Monodisperse Sulfonated Polystyrene Latex. *Langmuir* **1998**, *14*, 204–213.

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