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Direct visualization of layer-by-layer self-assembled multilayers of organometallic polymers

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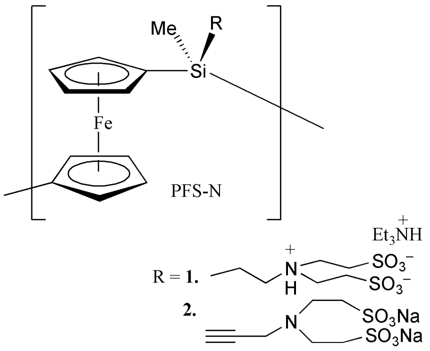
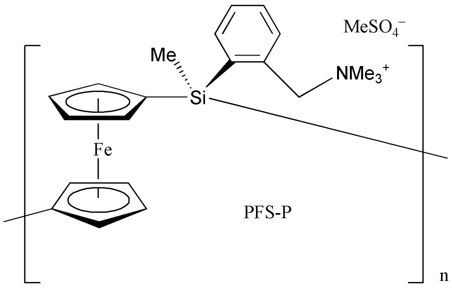
Direct visualization of organometallic-organic and novel all-organometallic multilayer superlattices prepared by layer-by-layer assembly of cationic/anionic polyferrocenylsilane and anionic polystyrene sulfonate polyelectrolytes using a gold coating/transmission electron microscopy (TEM) technique is reported.

Electrostatic superlattices formed through layer-by-layer (LbL) self-assembly of oppositely charged polymers have been of intense interest since the concept was first reported by Decher in 1991.[1] Depending on the polyelectrolytes used, one can tailor the chemical and physical properties of these ultra-thin film assemblies for a range of applications.[2] To date, the vast majority of polymers chosen for such multilayer superlattices have been organic. Organometallic polymers such as polyferrocenylsilanes (PFSs)[3] offer additional possibilities for creating structures with interesting redox, conductive, or preceramic properties.[4] With the development of water-soluble PFS polyelectrolytes,[5,6] we have been able to extend such purely organic polymer superlattices to examples based on organometallic PFS and organic polymers[7,8] and, for the first time in this communication, we describe layer-by-layer assemblies based entirely on organometallic polymers.

To date, LbL multilayer superlattices have mainly been characterized by indirect routes. These include ellipsometry, Quartz Crystal Microbalance studies, XPS, UV-vis, and AFM.[1,2] Recently, inorganic nanocrystals formed within the nanoscale spaces of organic polyelectrolyte superlattices have been used to locate interfaces between multilayer blocks by transmission electron microscopy (TEM).[9] In this communication we demonstrate that a thin gold layer deposited on the top surface of an organometallic polymer superlattice provides a straightforward means of directly visualizing the layer-by-layer growth of multilayers by TEM. This method allows the effect of polymer structure, composition, and charge density on superlattice thickness to be established and moreover the gold–superlattice–gold sandwich architecture involving the redox-active PFS materials may enable construction of ultra-thin film devices.

Two LbL systems were investigated in this work: one involving a positively charged organometallic polyelectrolyte (**PFS-P)** coupled with negatively charged polystyrene sulfonate (**PSS**); and the other involving both the positively charged **PFS-P** and a negatively charged (**PFS-N**) organometallic polyelectrolyte. Owing to the water-solubility of both polymers, each can be individually incorporated into an electrostatic superlattice either with an oppositely charged organic polyelectrolyte or together in an all-organometallic assembly. Such lattices can be grown on a variety of different substrates which include, but are not restricted to, gold, quartz, and silicon. Initially, gold substrates were primed with an acid thiol such as 11-mercaptoundecanoic acid imparting a negative charge to the gold surface. The primed substrates were subsequently treated with a positive polyelectrolyte[10] which adheres due to the strong electrostatic attraction between the opposite charges. Once the primed gold surface had been compensated with positive charge the substrate was washed, dried, and transferred to a vial containing the negative polyelectrolyte. This cycle can be repeated until the desired number of multilayers are achieved which can range in number from a few to literally hundreds. After the deposition process was complete, the sample was sputtered with a thin film of gold. This was performed as there is no intrinsic electronic contrast between the multilayer film and surrounding medium needed for visualization techniques such as TEM. The additional layer of gold sputtered on top of the film provides this contrast. Fig. 1 shows TEM cross-





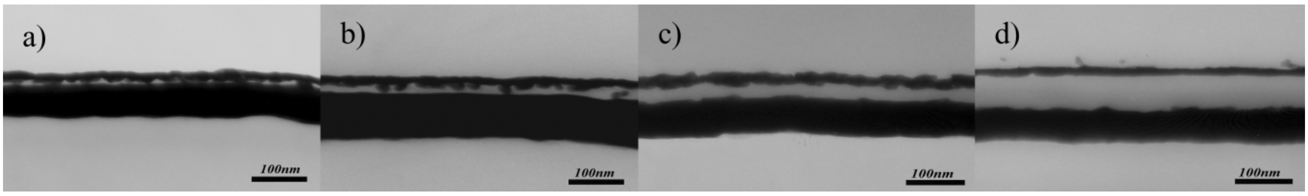


Fig. 1 TEM images for (a) 5, (b) 10, (c) 20, and (d) 30 bilayer films of PFS-P/PSS.

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sectional images of multilayer films consisting of 5, 10, 20, and 30 bilayers of alternating **PFS-P** and **PSS**. Significantly, the uneven and somewhat spotty coverage of the first several multilayers, which has been reported by others[11] for all organic superlattices and by ourselves[7] for **PFS-P**/**PSS** LbL systems based on indirect methods, can be clearly seen in the 5 bilayer superlattice and the effect is still apparent to a lesser extent in the 10 bilayer assembly. By the time 20 and 30 bilayer lattices have been prepared, one can visually follow the regular increase in multilayer thickness.

Another interesting aspect of LbL assemblies which can be readily investigated by the direct visualization technique we report herein is the influence of the charge density of the constituent polyelectrolytes on superlattice thickness. As **PSS** contains the single negative charge per repeat unit in a smaller volume than the organometallic **PFS-N1** counterpart, one would expect less **PSS** material to be required to compensate the underlying positive charge, which should ultimately result in a thinner film. To allow comparison, a 20 bilayer film of the previously reported **PFS-P/PSS** combination was compared to a 20 bilayer film of **PFS-P/PFS-N1** on a gold substrate. The layer-by-layer growth of the novel all-organometallic systems **PFS-P/PFS-N** on quartz was monitored by UV-vis spectroscopy in a manner similar to that previously reported for the **PFS-P**/**PSS** counterpart.[7] Fig. 2 shows, as an example, UV-vis spectra corresponding to 10 layers. Absorbances characteristic of PFS are observed as an intense ligand-to-metal charge-transfer (LMCT) at 220 nm and the weaker d–d band centered at 420 nm. The linear increase in the absorbances at these wavelengths indicate a regular increase of adsorbed polyelectrolyte with each layer. After gold was sputtered on the resulting superlattices TEM images (Fig. 3) clearly showed that the all-organometallic lattice is significantly thicker than the organic-organometallic lattice as anticipated.

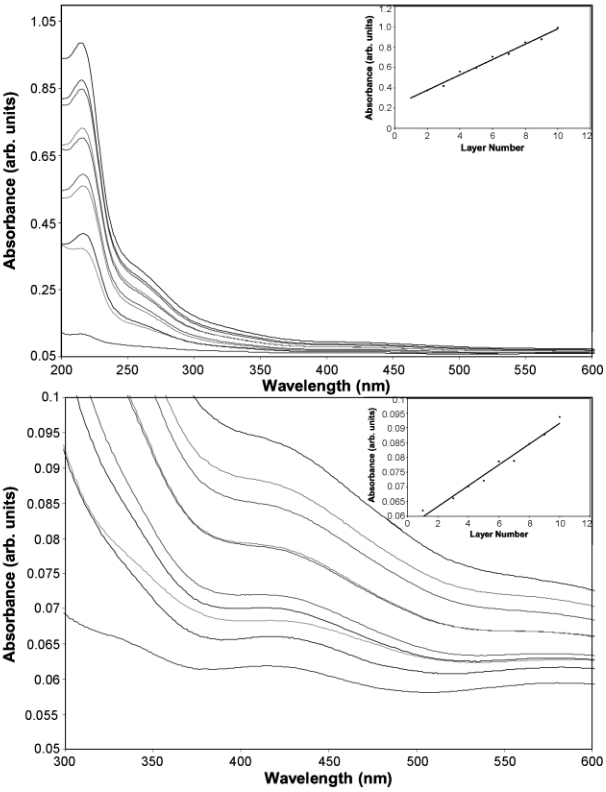

Fig. 2 UV-vis spectra for PFS-P/PFS-N2 multilayers corresponding to layers 1 to 10. (a) Region of the UV-vis spectra showing the PFS LMCT at ~220 nm. (b) Scale-expanded spectra showing the PFS d–d transition at ~420 nm. Insets show the systematic increase in absorbance with layer number at (a) 220 nm and (b) 420 nm.

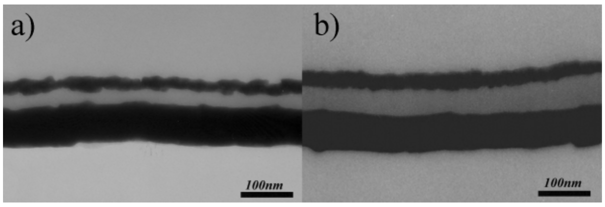

Fig. 3 TEM image for 20 bilayers of (a) **PFS-P**/**PSS** and (b) **PFS-P**/**PFS-N1** showing the effect of charge density on layer thickness.

In summary, in this preliminary communication we report (i) a facile and convenient way to monitor multilayer growth in self-assembled superlattices involving coating with gold followed by visualization of cross-sections by TEM and (ii) the first all-organometallic superlattice system which is of particular interest for the creation of nanoscale devices based on redox-active PFS materials. The direct visualization technique described should prove useful to probe many aspects of LbL assembly. Furthermore, pyrolysis of PFS superlattices may lead to the formation of magnetic multilayers[12] and this process could also be followed in a similar manner. Further studies will be reported in the near future.

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