Fluorinated polyphosphazenes (FPs) offer important advantages as biocompatible coatings for coronary stents and other biomedical devices. Recently, a new class of FPs has been introduced, which integrates carboxylic\(^1\) or sulfonic acid\(^3\) and fluorinated moieties into a single macromolecular structure. Assemblies of such fluorinated polyelectrolytes with polyelectrolytes or charged small functional molecules can offer efficient modulation of hydrophobicity, improved biocompatibility, as well as biofunctionality, such as modulated drug release. Here, we have explored aqueous multilayer polyelectrolyte deposition as a convenient route to nanofabrication of layered coatings built from ionic FPs (iFPs) and polyelectrolytes\(^1\) or small molecule partners. The resulting layer-by-layer (LbL) assemblies displayed controlled film growth, modulated hydrophobicity, swelling, and protein adsorption characteristics. Hydrophobic interactions largely contributed to the formation of LbL films of iFPs with polycations, leading to linear growth and extremely low water uptake. As shown in neutron reflectometry (NR) studies, films of fluorinated polyphosphazenes demonstrated superior layering and persistence of such layering in salt solution as compared to control nonfluorinated polyphosphazene/polycation films. Hydrophobicity-enhanced ionic pairing between iFP and linear polycations gave rise to large-amplitude oscillations in surface wettability as a function of capping layer. Importantly, hydrophobicity of iFP-capped LbL coatings could be further enhanced by using a highly porous polyester surgical felt rather than planar substrates for film deposition.\(^2\)

Moreover, because of the unique combination of ionic and hydrophobic properties, iFPs enabled direct LbL assembly with cationic antibiotics at neutral pH – a feature not achievable with traditional synthetic or biological hydrophilic polymers. The amount of antibiotics included in the coatings could be precisely tuned by coating composition and thickness. Importantly, antibiotics could be retained within the coatings for at least 30 days, and released in response to a trigger that indicated the onset of bacterial colonization, such as locally induced acidification. In addition, the coatings have demonstrated extremely low hemolytic activity (<1%), and were nontoxic to fibroblasts. Taken together, the data suggest that iFPs are versatile building blocks for creating surface coatings with controllable interfacial adhesion, wettability, and programmable interactions with biological milieux, including bacteria-triggered release of antimicrobials for prevention of bacterial colonization of surfaces.

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References