Coatings that prevent or decrease fouling are sought for many applications, including those that inhibit the attachment of organisms in aquatic environments. To date, antifouling coatings have mostly followed design criteria assembled over decades: surfaces should be well/strongly hydrated, possess low net charge and maintain a hydrophilic character when exposed to the location of use. In a major paradigm shift, this work describes antifouling glassy films made from certain complexes of positive and negative polyelectrolytes. The close proximity of equal numbers of opposite charges within these complexes mimics zwitterionic structures. Films, assembled layer-by-layer from aqueous solutions, contained sulfonated poly(ether ether ketone), SPEEK, a rigid polyelectrolyte which binds strongly to a selection of quaternary ammonium polycations. Surfaces coated with these films in the 100 nm thickness range completely resisted adhesion of the algae.