

### **Captions of Supporting Materials**

1. The  $^1\text{H}$ -NMR spectra of azo polyelectrolytes and corresponding azo compounds: (a) NAP, NAPE and PNAPE; (b) PAP, PAPE and PPAPE; (c) EAP, EAPE and PEAPE.
2. Atomic force microscopy (AFM) images of the substrate and multilayer film, (a) quartz slide surface, (b) PEAPE/PDAC multilayer (DF=11.8%, 30 bilayers).