The unique capability of PiFM to detect chemical species from the top surface of a sample is demonstrated in Fig. 1 where PS-b-PTMSS [poly(4-trimethylsilylstyrene)] block copolymer (BCP) "islands" and "holes" with horizontal lamellae are imaged. AFM topography images (Fig. 1(a) and Fig. 1(a')) confirm the island and hole structures as schematically depicted by Fig. 1(d) and Fig. 1(d') respectively. Each chemical block from the PS-PTMSS BCP has a thickness of 5.5 nm (Fig. 1(f)). The islands (holes) should have PTMSS (PS) as the top element whereas the areas surrounding the islands (holes) have PS (PTMSS) as the top element as shown in Fig. 1(d) (Fig. 1(d')). However, given the size of the features, there is no adequate analytical technique that can confirm such structure with confidence. The PiFM image at a PS vibrational band 1493cm⁻¹ (PTMSS vibrational band 1599cm⁻¹) in Fig. 1(b) (Fig. 1(c')) shows that the regions surrounding the islands (holes). Likewise, the PiFM image at a PTMSSS vibrational band 1599cm⁻¹ (PS vibrational band 1493cm⁻¹) in Fig. 1(c) (Fig. 1(b')) shows that the islands (holes). Likewise, the PiFM image at a PTMSSS vibrational band 1599cm⁻¹ (PS vibrational band 1493cm⁻¹) in Fig. 1(c) (Fig. 1(b')) shows that the islands (holes) are populated by PTMSS (PS) molecules and thus appear bright compared to the islands (holes). Likewise, the PiFM image at a PTMSSS vibrational band 1599cm⁻¹ (PS vibrational band 1493cm⁻¹) in Fig. 1(c) (Fig. 1(b')) shows that the islands (holes) are populated by PTMSS (PS) molecules. This chemical information is overlaid on top of the 3D topography in Fig. 1(f) and 1(f') showing an excellent correlation to the schematic structure shown in Fig. 1(d) and 1(d').



FIGURE 1. (a) and (a') AFM topography of "island" and "hole" structures of PS-PTMSS BCP. (b) and (b') PiFM images acquired at 1493 cm⁻¹, which highlights PS molecules. (c) and (c') PiFM images acquired at 1599 cm⁻¹, which highlights PTMSS molecules. (d) and (d') Schematic cross-sectional drawing of the island and hole structure. (e) and (e') Chemical map overlaid on 3D AFM topography. (f) 3D topography overlaid with chemical mapping information.