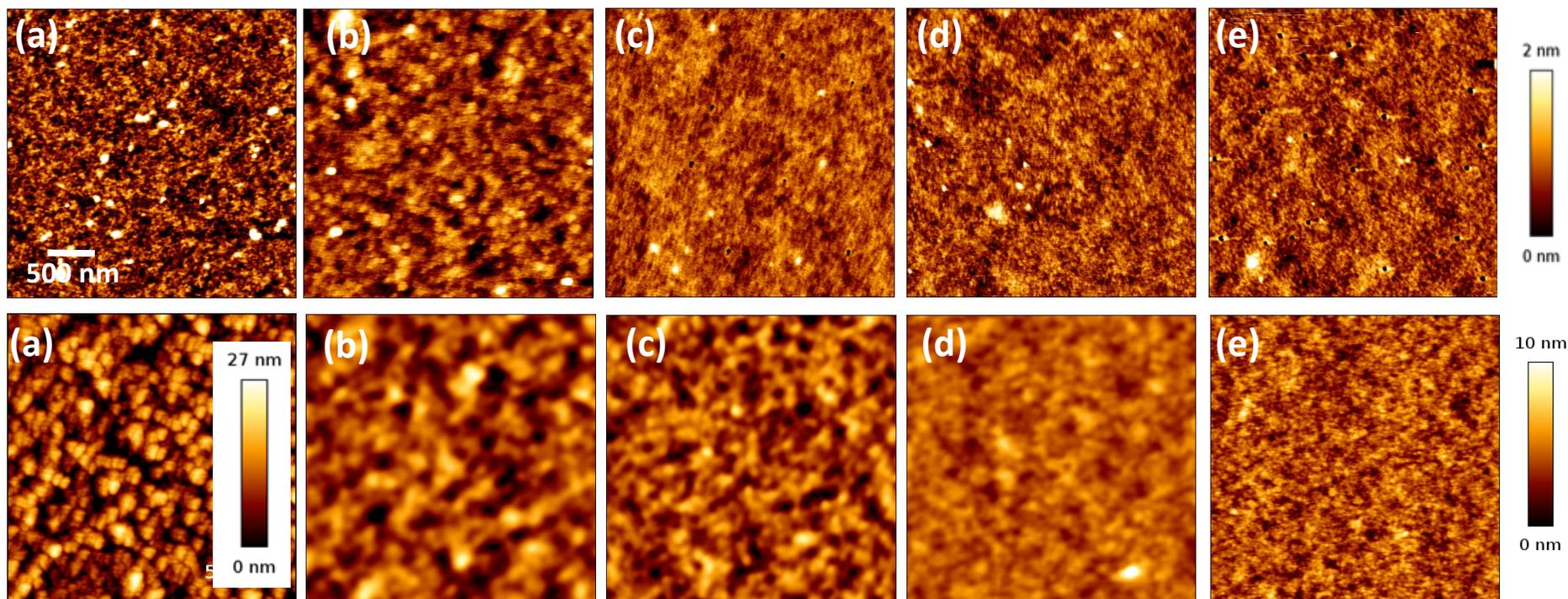
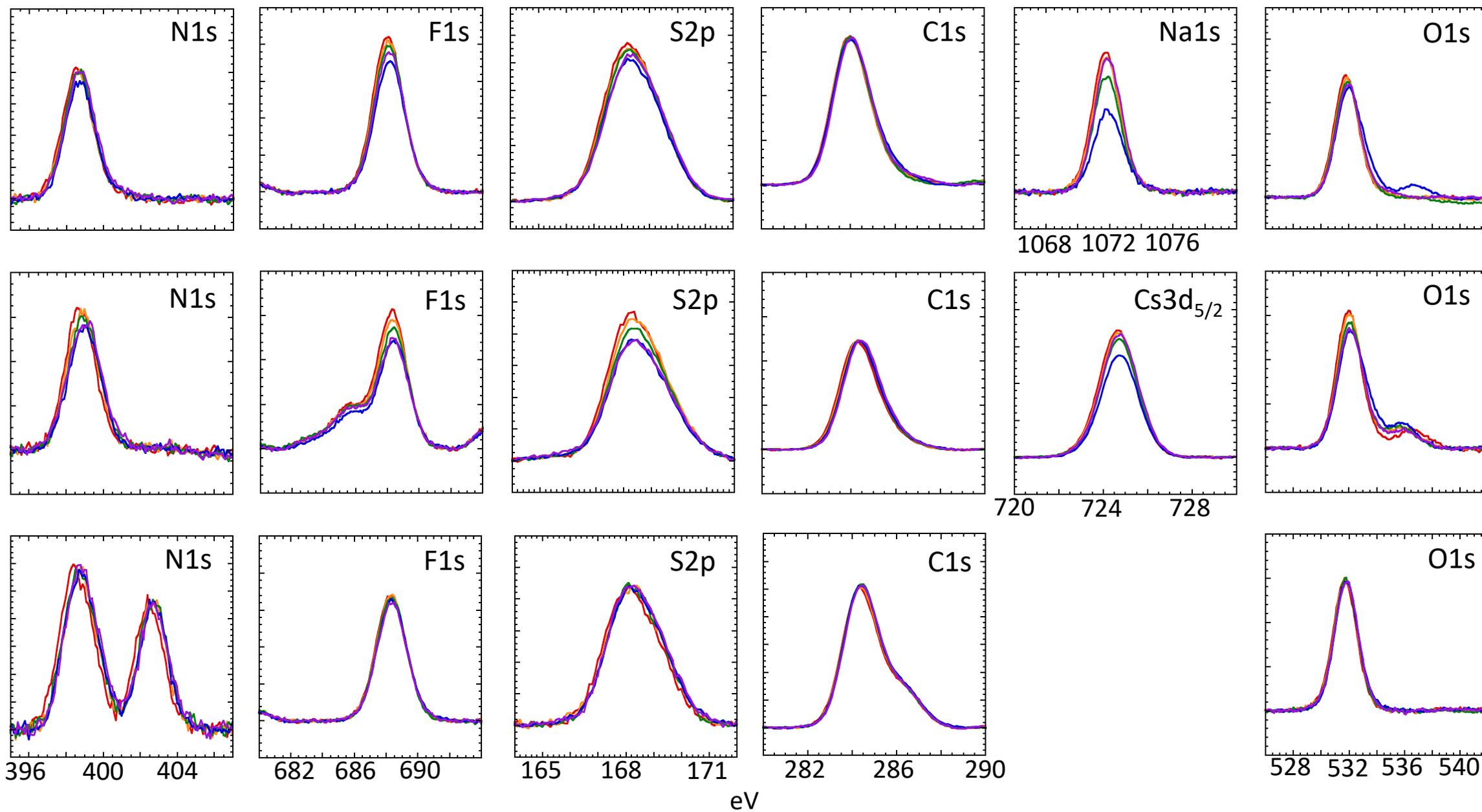


Supplementary Figure S1. Core-level X-ray photoemission spectra of TFB-CF₃SIS-M. M= Li, Na, Cs. **(a)** TFB-CF₃SIS-Na: The experimental elemental ratios of N1s: S2p: F1s: Na1s: C1s are 3.0: 4.3: 5.6: 2.2: 45 (c.f. theoretical ratio of 3 : 4 : 6 : 2 : 43). **(b)** TFB-CF₃SIS-Cs: The experimental elemental ratios of N1s: S2p: F1s: Cs3d: C1s: are 3.0: 4.3: 5.4: 2.1: 43.5) (c.f. theoretical ratio of 3: 4: 6: 2: 43). No observable intensity for Na1s. **(c)** TFB-CF₃SSI-Li: The experimental elemental ratios of N1s: S2p: F1s: C1s: are 3.0: 4.3: 5.6: 45) (c.f. theoretical ratio of 3: 4: 6: 43). No observable intensity for Na1s. Experimental ratios fall within ±10% of theoretical ratio, within the quantification error limits. In a separate experiment, TFB-CF₃SIS-Li and Na solid samples are digested in conc. HNO₃, and metal cations content were quantified using inductive coupling plasma-optical emission spectroscopy (ICP-OES). For Li TFB-CF₃SIS-Li sample, Li was determined to be 0.99 %wt/wt (Theo. 1.4% wt/wt). Only residual Na 0.04 %wt/wt was detected. This is consistent with XPS results. Reference TFB-CF₃SIS-Na, Na was determined to be 3.3 % wt/wt (Theo. 4.53 % wt/wt).

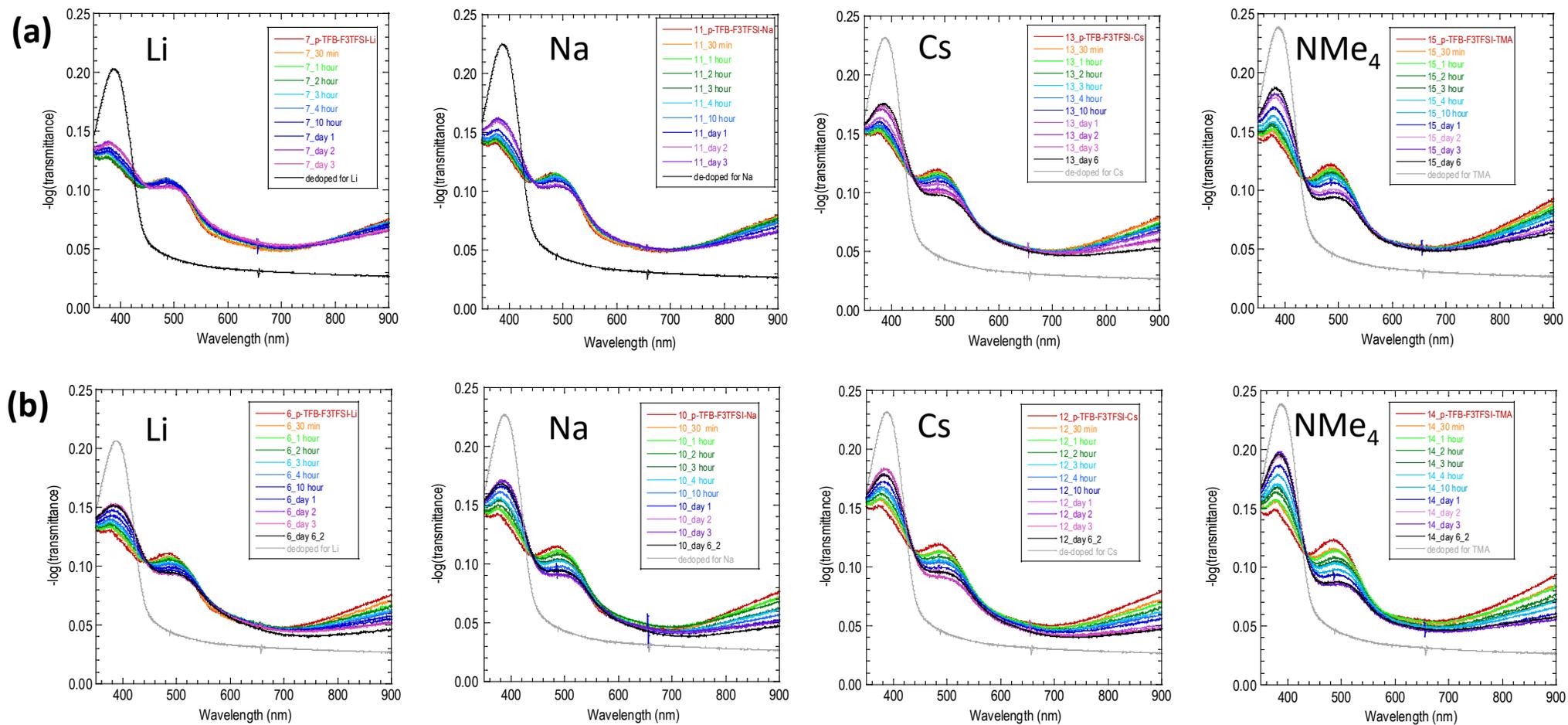


Supplementary Figure S2. 3x3 μm atomic force microscopy images of pristine and SC hole-doped TFB-CF₃SIS-M films. **Top panel:** 70-110-nm thick TFB-CF₃SIS-M films were spin-cast onto oxygen-plasma treated Si substrates from 20 mM polymer in ACN **(a)** 95-nm-thick film TFB-CF₃SIS-Li rms roughness = 0.47 nm **(b)** 88-nm-thick TFB-CF₃SIS-Na rms roughness = 0.36 nm **(c)** 77-nm-thick film TFB-CF₃SIS-Cs roughness rms= 0.26 nm **(d)** 70-nm-thick film TFB-CF₃SIS-NMe₄ rms roughness = 0.31 nm **(e)** 110-nm-thick film TFB-CF₃SIS-NEt₄ rms roughness = 0.34 nm. **Bottom panel:** 30-40-nm thick hole-doped TFB-CF₃SIS-M films were spin-coated onto oxygen-plasma treated Si substrates from 0.45 μm nylon filtered 15 mM polymer in ACN **(a)** 40-nm-thick film TFB-CF₃SIS-Li rms roughness = 5.3 nm **(b)** 30-nm-thick TFB-CF₃SIS-Na rms roughness = 1.5 nm **(c)** 42-nm-thick film TFB-CF₃SIS-Cs rms roughness = 1.4 nm **(d)** 40-nm-thick film TFB-CF₃SIS-NMe₄ rms roughness = 0.8 nm **(e)** 30-nm-thick film TFB-CF₃SIS-NEt₄ rms roughness = 0.7 nm. Tapping-mode AFM.

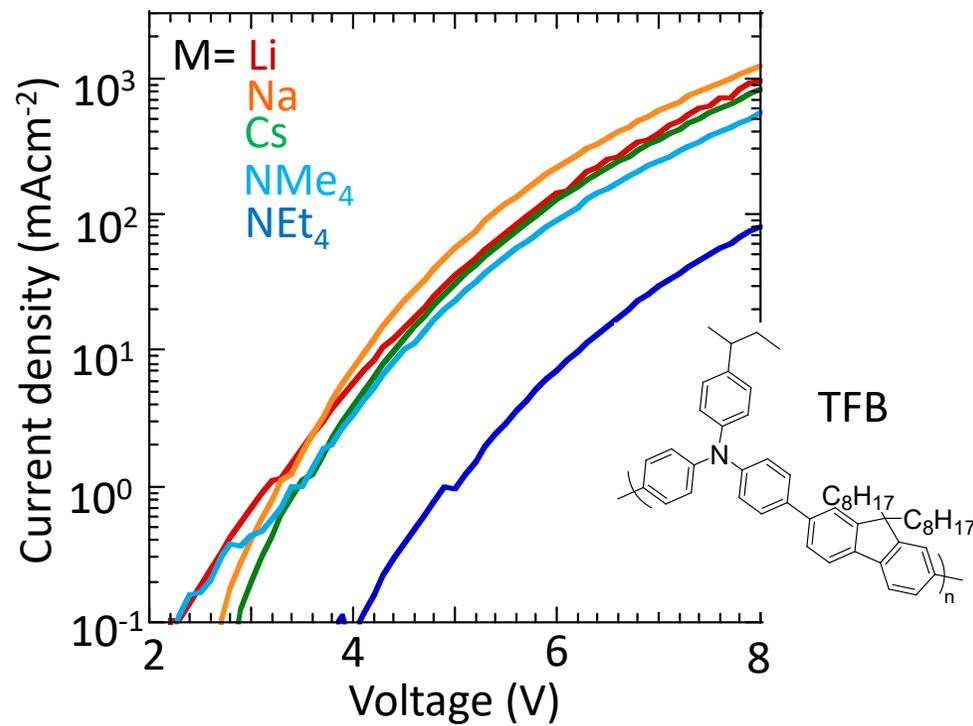
Photoemission intensities



Supplementary Figure S3. Variable-angle XPS core-level spectra of TFB-CF₃SIS-M for M=Na, Cs and NMe₄. **Top panel:** M=Na. **Middle panel:** M=Cs. **Bottom panel:** M=NMe₄. Photoemission angle θ is the direction of the electron analyzer axis from film normal. Excitation, Mg K $_{\alpha}$ (1253.6 eV). Run sequence: $\theta = 0^{\circ}$ (red), 20° (orange), 40° (green), 60° (blue); 0° (purple). To correct the intensity for the small X-ray induced damage $\theta = 0^{\circ}$ was repeated at the end. All spectra have been background corrected using linear functions across the elastic photoemission peak. C1s is used as internal reference because the carbon atom concentration is practically constant in these organic polymer films.



Supplementary Figure S4. Optical spectra of TFB-CF₃SIS-M as a function of time. (a) N₂ (298 K, 1ppm H₂O) (b) ambient (298 K, 65% RH). M = Li, Na, Cs and NMe₄.



Supplementary Figure S5. Current density–Voltage curves for organic diodes with SC hole-doped TFB-CF₃SIS-M as hole injection layer (HIL) after baking at 120°C 5 min in N₂ glovebox (298 K, 1ppm H₂O). 100-nm-thick TFB as semiconductor, TFB-CF₃SIS-M as hole-injection layers and Al as top-electrode.