Supporting Information

During UPS measurements, radiation-induced damages due to high-energy photon flux and scattering of outcoming photoelectrons commonly occur, thus permanently altering electronic properties of organic molecules (energy level position, band width, switching). Here, to determine the influence of radiation damage on the spectra data, we compared the UPS spectra of DAE1-o film (on ITO glass) measured with and without Al filter. The results were shown in Fig. S1. It is obvious that radiation induced changes took place within 10 min when the measurements were performed without filter; however, these changes could be avoided with using an Al filter.

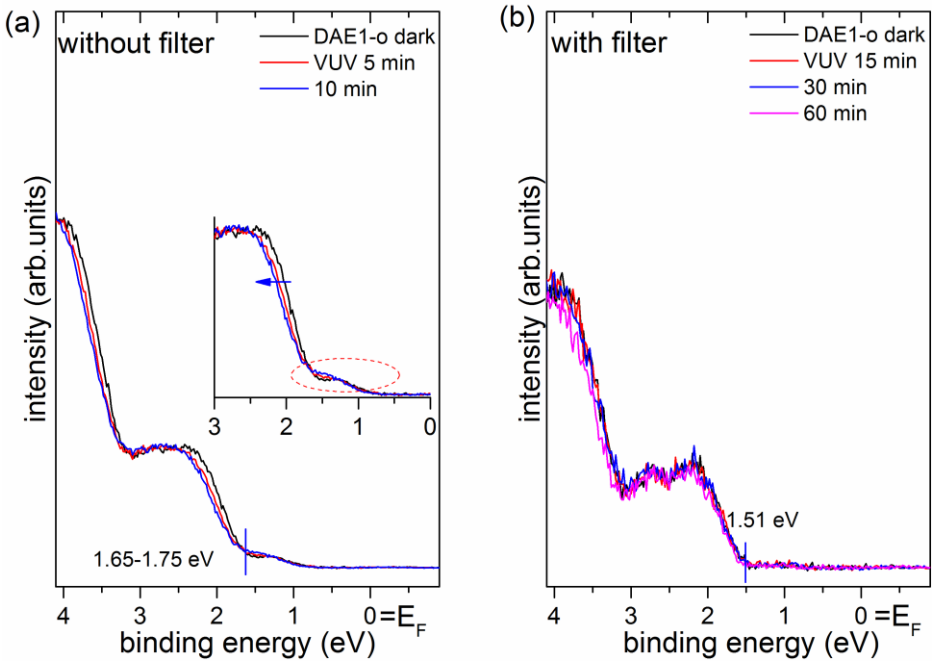

Figure S1. HeI radiation-induced damage, HeI UPS spectra of DAE1-o film (10 nm) on ITO glass before (DAE1-dark) and after prolonged HeI light (VUV) irradiation: (a) HeI light with strong photon flux from a standard commercial light source; obvious radiation damage (shift, switching, charging) could be seen even in a short-time irradiation (5 min), which is almost the same as a typical acquisition time of UPS spectra. (b) Photon flux of HeI was attenuated to ca. 20 times using a Al thin film filter (ca. 500 nm), with which no obvious spectra shift or switching were observed within 1 h irradiation.

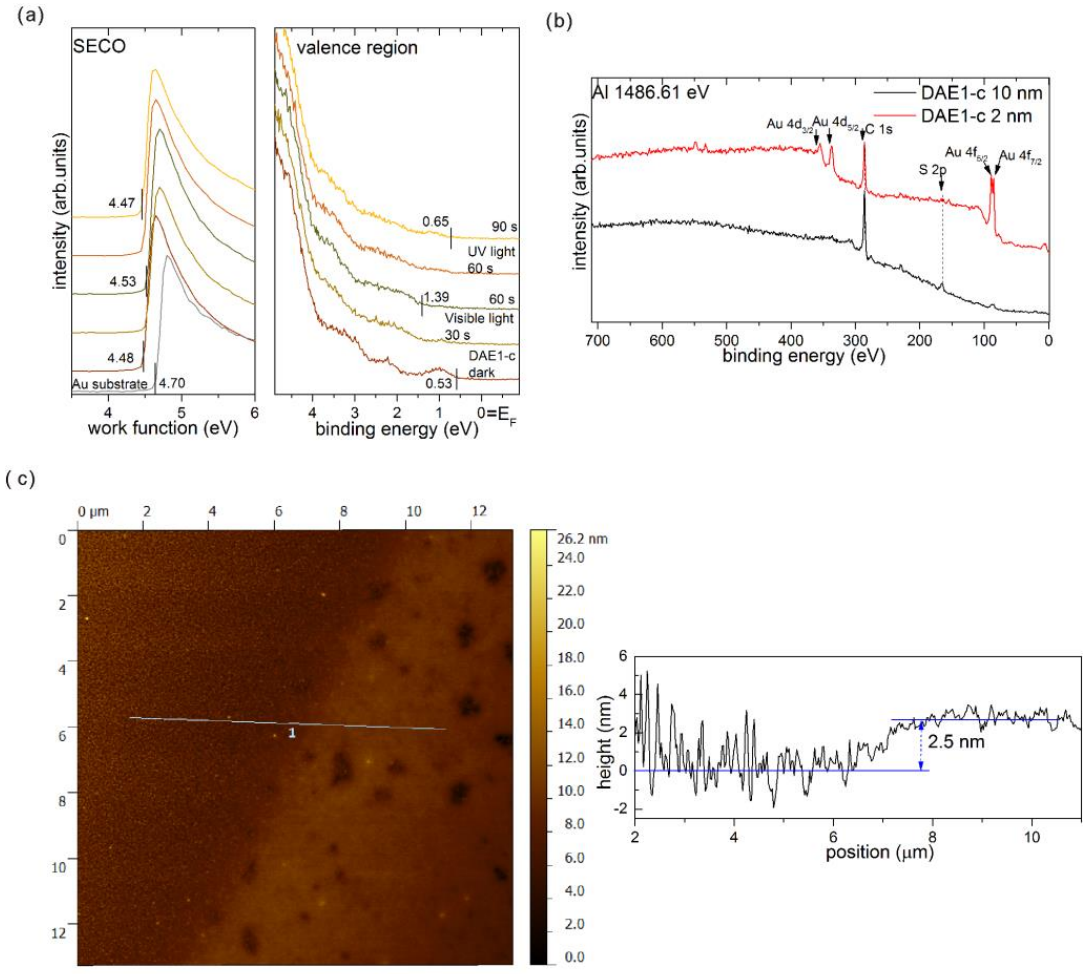

Figure S2. (a) UPS spectra of 2 nm DAE1-c film, switching process was achieved by the irradiation of visible and ultraviolet light, respectively. (b) XPS survey spectra of thick and ultra-thin DAE1-c film deposited on Au substrate. The signals of gold (e.g., Au 4f) indicate film thickness differences. (c) Topography image of ultra-thin DAE1-c layers on Au surface as measured by AFM. Film thickness was measured by partially wiping away surface molecules using ethanol.

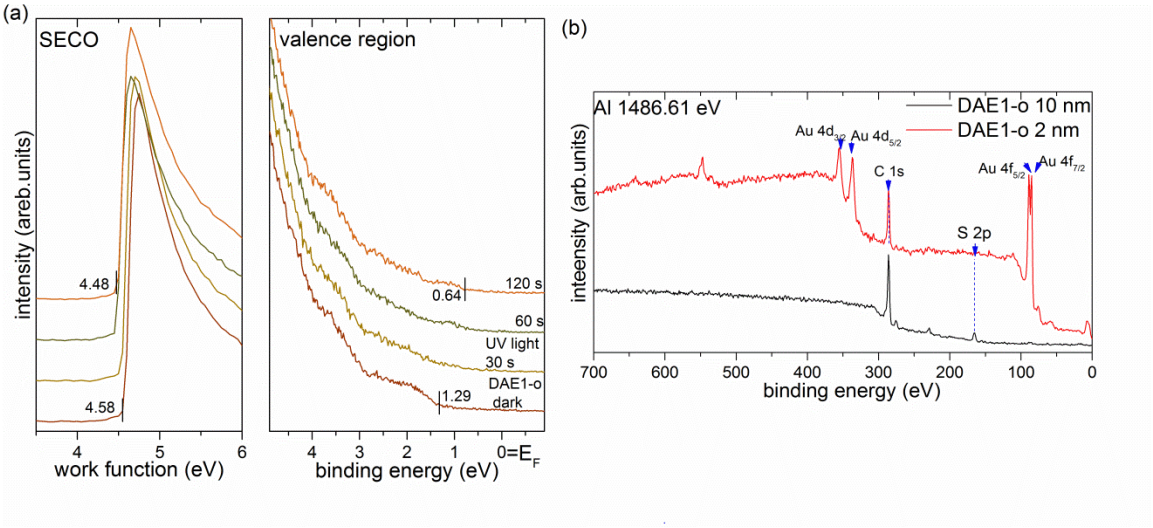

Figure S3. (a) UPS spectra of 2 nm DAE1-o film, switching process was achieved by the irradiation of UV light. (b) XPS survey spectra of thick and ultra-thin DAE1-o film deposited on Au substrates.

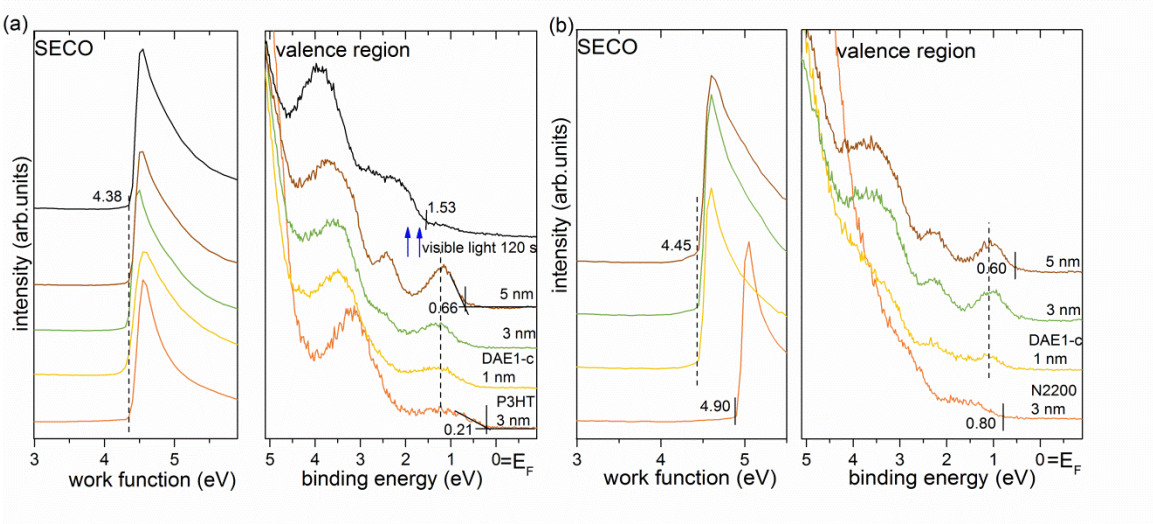

Figure S4. (a) UPS spectra of DAE1-c films with incremental deposition thickness on P3HT substrates. After 5 nm thick deposition, samples were irradiated by visible light (λ>450 nm); during this process, molecules switched from closed to open form. (b) UPS spectra of DAE1-c films with incremental deposition thickness on N2200 substrates.

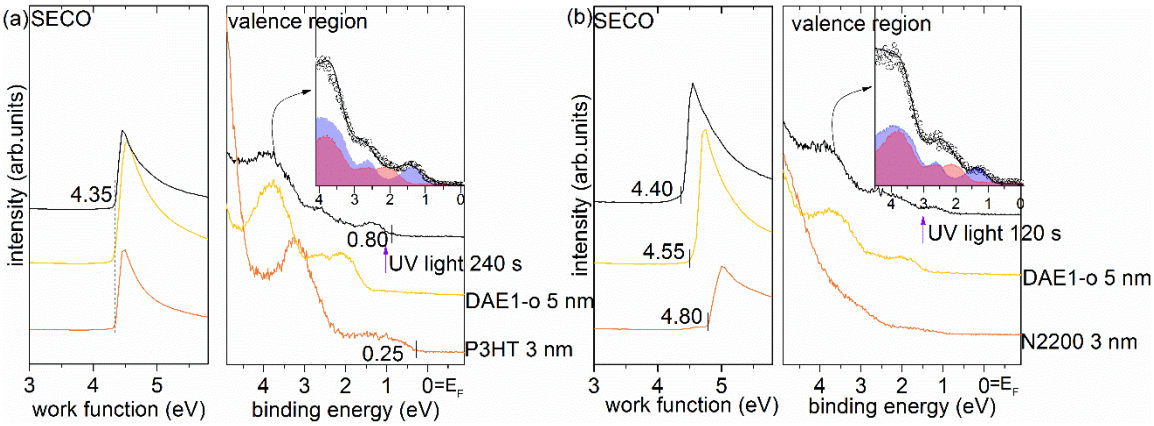

Figure S5. UPS spectra (valence and SECO regions) of 5 nm thick DAE1-o films on (a) P3HT and (b) N2200, and light switching induced changes. Inset: deconvolution of sample spectrum (open circles) after UV light irradiation with DAE1-c and DAE1-o contributions (sum given by the black line, which is composed by 45% of DAE1-o and

55% of DAE1-c components for films on P3HT substrates, and 50% of DAE1-o and 50% of DAE1-c components for films on N2200 substrates).

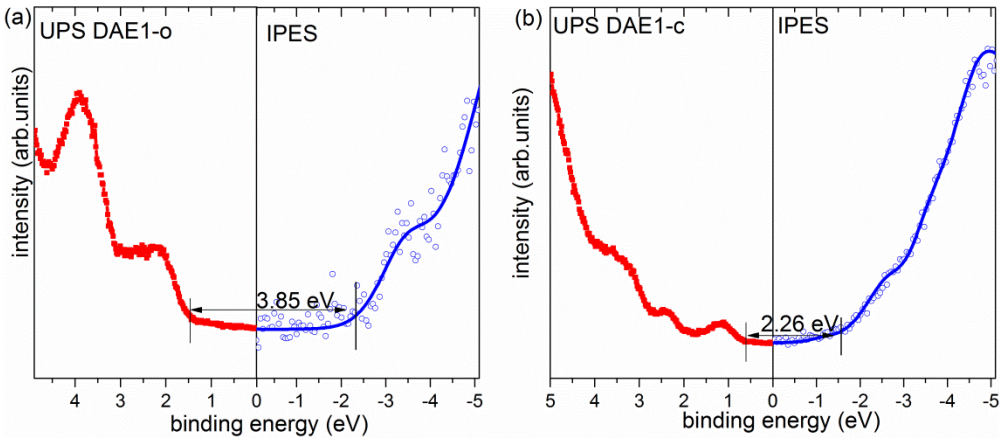

Figure S6. UPS / IPES spectra of 10 nm (a) DAE1-o, (b) DAE1-c films on ITO substrates, from which the charge transport gaps (3.85 eV for DAE1-o, 2.26 eV for DAE1-c) of the DAE1 layers were determined. For the IPES measurement, the sample and filament current were kept at an extremely low level (I_{sam} < 0.1 μA, $I_{filament}$ =1.03 A) to minimize sample damage.