# Electronic Supplementary Information

## Utilizing Diels-Alder "Click" Chemistry to Functionalize the Organic-Organic Interface of Semiconducting Polymers

*David Burmeister, Lukas Ahrens, Andreas Opitz, Giovanni Ligorio, Felix Hermerschmidt, Daniel Jänsch, Jan Freudenberg*, Uwe H. F. Bunz, Klaus Müllen and Emil List-Kratochvil**

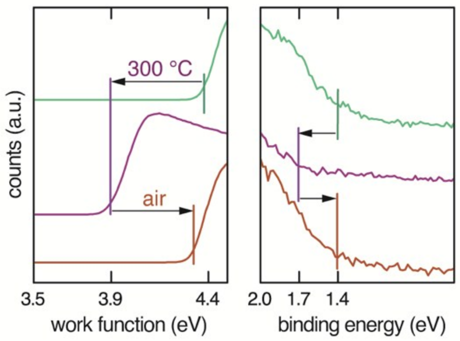

**Figure S1.** SECO (left) and HOMO onset (right) of **PF** films in inert conditions after spin-coating, after cross-linking and cross-linked exposed to ambient conditions for 1 h. The almost entirely reversible changes are most likely due to water and oxygen de- and adsorption.

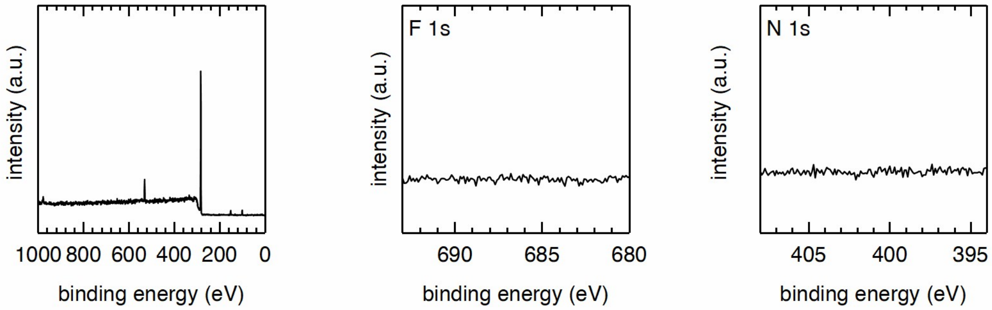

**Figure S2.** XPS spectrum of **PF** cross-linked. Survey (left), signal of F 1s core level (middle) and signal of N 1s core level are shown. The survey shows the presence of oxygen (531 eV, O 1s) as was observed for non-cross-linked samples (not shown). F 1s is nonexistent since there is no fluorine in **PF**. A N 1s signal from the end groups of the polymer was not observed.

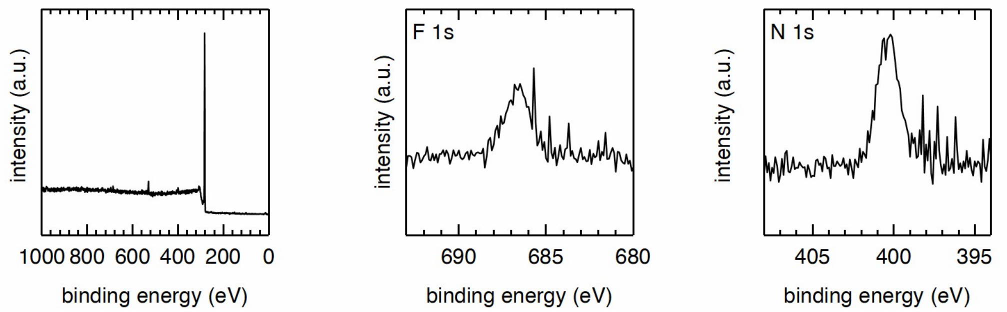

**Figure S3.** XPS spectrum of **PF** cross-linked and functionalized with **4F-PTAD**. Survey (left), signal of F 1s core level (middle) and signal of N 1s core level are shown. F 1s and N 1s signals are found in the expected 1:3 ratio.

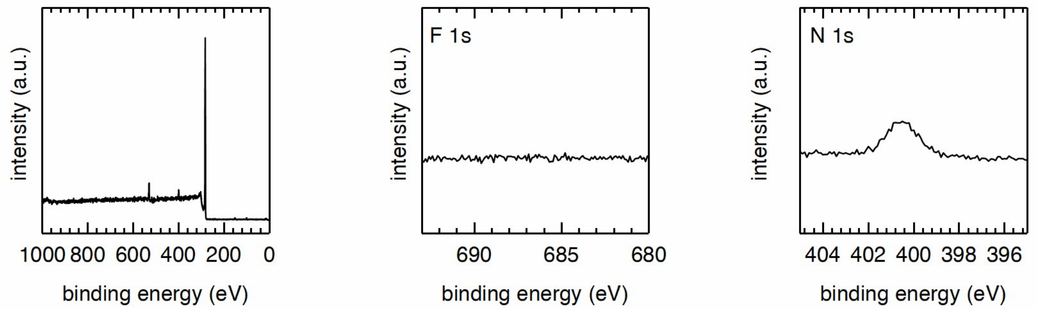

**Figure S4**. XPS spectrum of **PF** cross-linked and functionalized with **PTAD**. Survey (left), signal of F 1s core level (middle) and signal of N 1s core level are shown. Nitrogen signal corresponding to the 3 nitrogen atoms contained in **PTAD** was found.

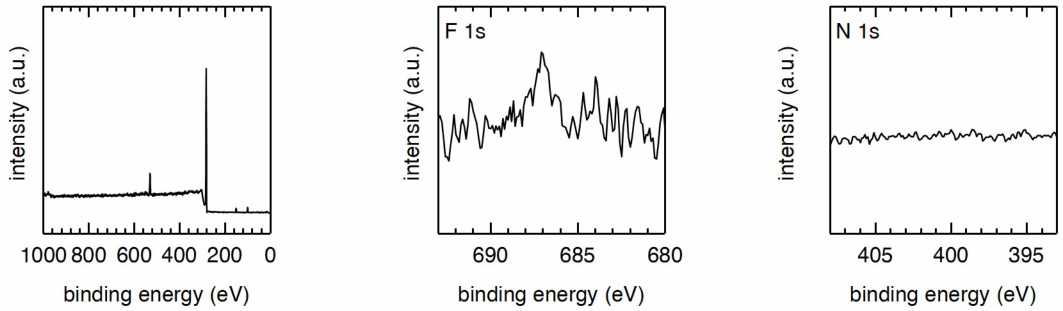

**Figure S5.** XPS spectrum of **PF** cross-linked and functionalized with **4F-PMI**. Survey (left), signal of F 1s core level (middle) and signal of N 1s core level are shown. The less potent *N*-phenylmaleimide dienophiles are hardly resolvable in the XPS experiment. A F 1s signal of 4F-*N*-phenylmaleimide was received. The single nitrogen atom of **4F-PMI** was not observed since the photoionization cross section of nitrogen is smaller than that of fluorine.

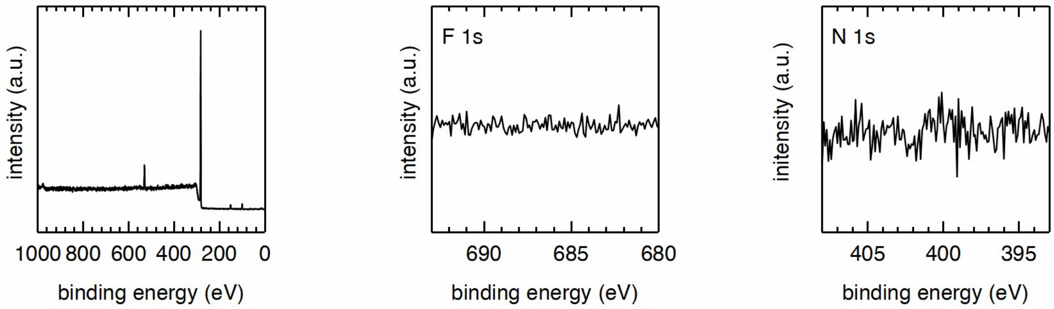

**Figure S6**. XPS spectrum of **PF** cross-linked and functionalized with **PMI**. Survey (left), signal of F 1s core level (middle) and signal of N 1s core level are shown. Functionalization with non-fluorinated *N*-phenylmaleimide, **PMI**, cannot be directly confirmed by XPS. However, since the reactivity of **4F-PMI** and **PMI** is expected to be similar, it is valid to assume the functionalization with **PMI** to a similar extent.

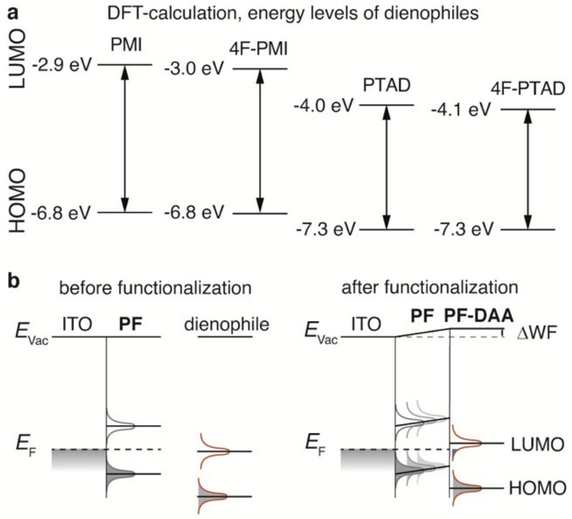

**Figure S7**. a) DFT-calculations were performed with B3LYP exchange correlation potential and ccpvtz basis set (as implemented in Gaussian 09). The higher the amount of electronegative atoms (nitrogen, fluorine), the lower the energy of the lowest unoccupied orbital (LUMO) of the corresponding structure. This corresponds to a higher electron affinity. The **PTAD** derivatives carrying two more nitrogen atoms than the **PMI** derivatives possess therefore a higher electron affinity. The fluorinated (**4F-PTAD**, **4F-PMI**) derivatives also show higher electron affinity in comparison to their respective non-fluorinated analogs (**PTAD**, **PMI**). b) Mechanism of Fermi Level pinning at acceptor LUMO. Highest occupied molecular orbital (HOMO) and LUMO distributions of the disordered polymer are illustrated as Gauss-distributions, the highest density of states is marked with a line and occupied states are greyed out. Left: Sample stack before functionalization and dienophile with high electron affinity. Right: Functionalization of **PF** with dienophiles results in **PF-DAA** at the sample surface. Due to the high electron affinity of the dienophile, the functionalization product resembles an acceptor. Tail states of the **PF-DAA** LUMO distribution are filled by charge transfer from the ITO electrode to the acceptor states. This results in an electric field and therefore a potential drop over the **PF** film. This potential drop corresponds to the vacuum level shift (ΔWF) and the observed work function increase due to film functionalization with electron withdrawing dienophiles.

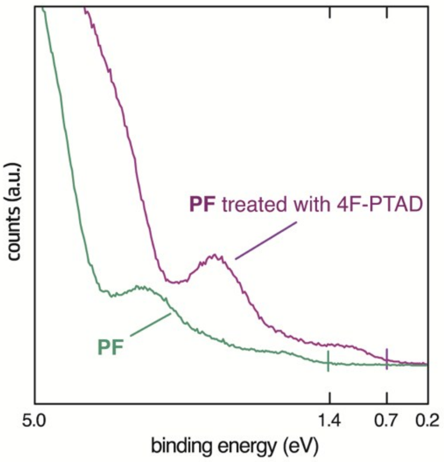

**Figure S8.** Valence band comparison between **PF** as spin-coated and **PF** cross-linked and functionalized with **4F-PTAD**. No additional photoelectron bands are observed in the **4F-PTAD** treated sample. This strengthens the conjecture of a covalent functionalization as opposed to a solely physical deposition of a film of acceptor molecules.

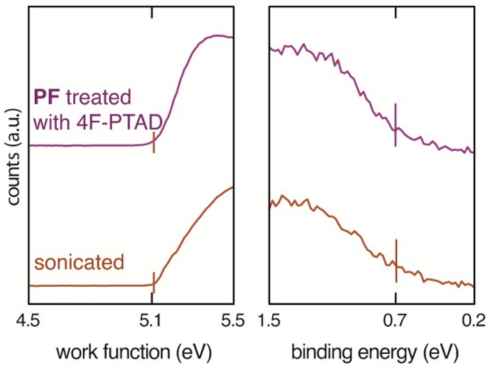

**Figure S9.** SECO (left) and HOMO onset (right) of cross-linked **PF** film functionalized with **4F-PTAD** before sonication and after sonication (toluene) in ambient conditions. The stability of the energy levels upon sonication confirm the covalent character of the functionalization. Once the dienophile is attached to the film it cannot be washed off.

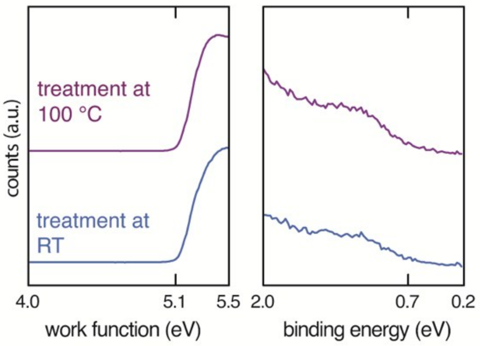

**Figure S10.** SECO (left) and HOMO onset (right) of **PF** films in inert conditions after functionalization with **4F-PTAD** at 100 °C, and room temperature (RT). The high reactivity of the nitrogen double bond enables reactions even at room temperature.

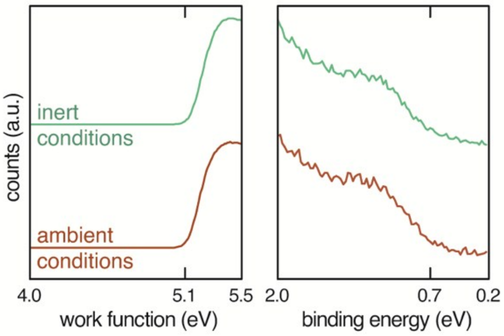

**Figure S11.** SECO (left) and HOMO onset (right) of cross-linked **PF** film functionalized with **4F-PTAD** in inert conditions and functionalized in ambient conditions. The same results were obtained for reactions conducted in inert conditions with dried solvents as for reactions in ambient conditions.

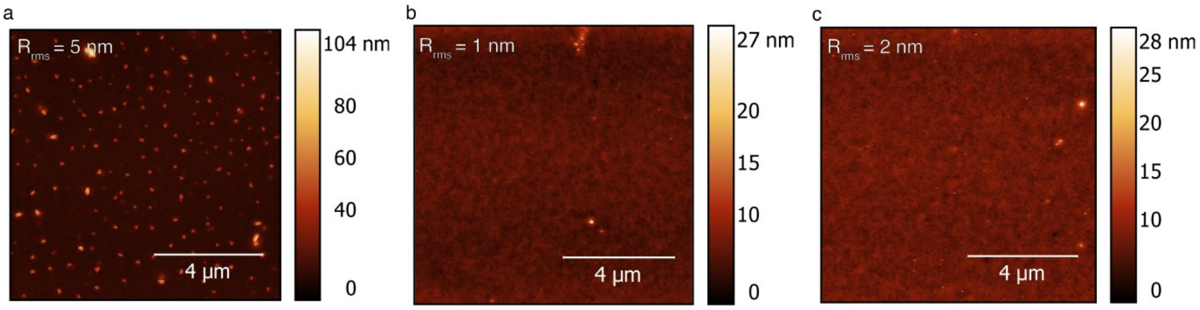

**Figure S12**. Scanning force microscopy images of **PF** films. Images were levelled, a polynomial background fit was conducted and the root mean square roughness was calculated with Gwyddion). a) **PF** film spin coated. Agglomerates show that parts of the polymer may have started to crosslink before the thermal treatment. With more material available, these agglomerates can be easily separated by filtration. b) **PF** film after cross linking at 300 °C for 1 h. c) **PF** film after treatment with **4F-PTAD** solution for 1 h at 100 °C.

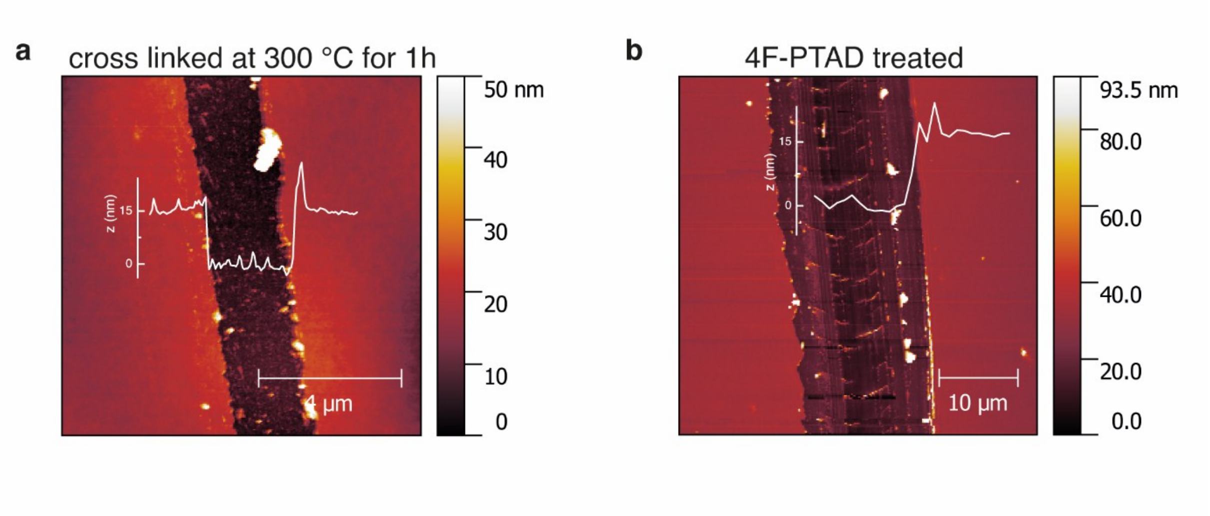

**Figure S13**. Scanning force microscopy images of **PF** films comparing the thickness of films before and after functionalization. a) A cross linked **PF** film with a scratch made to determine the film thickness. The step indicates a thickness of 15 nm. b) A cross-linked and subsequently **4F-PTAD** treated film scratched to determine the film thickness. The film thickness still shows to be 15 nm. This proves that the cross-linking procedure is suited to withstand the reaction conditions of the functionalization (100 °C, toluene).

## Experimental methods

*Preparation of films*: The films were prepared in inert conditions if not stated otherwise. By spin-coating 10 µL (1000 rpm, 60 s) of **PF** dissolved in toluene (5 mg/mL) films of about 60 nm thickness were produced. For optical characterization 2×2 cm cover slips (ROTH) were used. For XPS and UPS experiments, 1×1 cm ITO-coated substrates were used. The film thickness was determined with an Olympus LEXT OLS4100 laser scanning microscope.

*Cross-linking of films*: The films were cross-linked in inert conditions. The spin-coated substrates were placed on a heating plate, covered with a petri dish and heated at 300 °C for 1 h.

*Functionalization of cross-linked films*: The cross-linked films were allowed to cool down to room temperature and subsequently placed in a 0.05 M toluene solution of the corresponding dienophile at 100 °C for 2 h. The films were removed from the solution, submerged in fresh toluene and rinsed with 10 mL fresh toluene each, if not stated otherwise.

*UPS experiments*: The UPS spectra were recorded in a lab-system consisting of an analysis chamber (base pressure: $1 \times 10^{-9}$ mbar) connected to a load-lock chamber (base pressure: $5 \times 10^{-8}$ mbar), using He I resonance line as excitation source. An Omicron EA125 hemispherical energy analyzer was used to collect the spectra. The SECO spectra were measured with a sample bias of –10 V to clear the analyzer WF. All measurements were performed at room temperature. The obtained values were rounded to one decimal place. The error of the method is ±0.1 eV. The WF was determined by linear fitting the background and the linear region of the SECO, and reading of the point of intersection. The HIB was determined by linear fitting the background and the valence band onset, and reading of the point of intersection.

*XPS experiments*: X ray photoemission spectroscopy (XPS) and XPS depth profiling was performed in a JEOL JPS 9030 photoelectron spectrometer system using the Al Kα (1486 eV) excitation source (monochromator was employed). Quantitative comparison was conducted by subtraction of a Shirley function, signal integration and multiplication with the corresponding photoionization cross section. XPS depth profiling was performed using the instrument's $Ar^+$ ion source (3 mA ion current with 300 V acceleration voltage). The samples were grounded both during sputtering and during the photoemission analysis.

*Optical characterization*: Ultraviolet-visible (UV vis) measurements of films were performed on cover slips with a PerkinElmer Lambda 950 spectrometer in standard transmission operation (1 nm step size, 800 - 300 nm scan range, Xe lamp). Photoluminescence measurements were performed with an Edinburgh Instruments FLS 980 spectrometer in inert atmosphere. The samples were prepared on microscopy cover slips.

*Scanning force microscopy (SFM)*: The sample surface morphology was measured using a scanning force microscope equipped with a *Bruker Dimension FastScan* system in tapping mode. Height and phase images were recorded using Al-coated silicon probes with a spring constant of 0.4 N $m^{-1}$. SFM data was evaluated using the *Gwyddion* program.