Supporting Information

Microporous polymer network films covalently bound to gold electrodes

Daniel Becker,†[a] Nina Heidary,†[b,d] Marius Horch,[b] Ulrich Gernert,[c] Ingo Zebger,[b] Johannes Schmidt,[a] Anna Fischer*[b,d] and Arne Thomas*[a]

[a] Department of Chemistry, Functional Materials, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin. [b] Department of Chemistry, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin [c] Center for Electron Microscopy (ZELMI), Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin. [d] Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstrasse 21, 79104 Freiburg.

Materials and methods

Gold coated silicon wafers of 10 cm in diameter and 0.5 mm in thickness were purchased from Sigma-Aldrich. The wafer exhibits an additional layer of titanium between silicon and gold to facilitate adhesion of the 100 nm thick gold film. According to product specifications the silicon shows an orientation of <100> and the gold is of polycrystalline nature with a preference to <111> orientation. Absolute ethanol was obtained from Carl Roth. Dry solvents were purchased from Acros Organics, tetraphenylmethane from Alfa Aesar. Bromine, bis(1,5-cyclooctadiene)nickel(0), 2,2'-bipyridyl and 1,5 cyclooctadiene were obtained from Sigma Aldrich. All chemicals were used as received. Tetrakis(4-bromophenyl)methane was synthesized according to literature procedures (see below).

Elemental analysis was carried out at a Thermo Flash EA 1112 Organic Elemental Analyzer, infrared spectroscopy at a Varian 640-IR FT-IR Spectrometer in ATR mode, solid-state NMR measurements at a Bruker Avance 400 MHz Solid State and nitrogen sorption investigations at a Quantachrome Instruments Autosorb-1. SEM measurements were performed with a HITACHI high-resolution FEG-SEM (model SU8030 or SU8220) operated between 5 and 10 kV. EDX analysis was performed with a TEAM EDX-System from EDAX (30 mm2 SDD).

Gold substrates were obtained by cutting a gold coated silicon wafer into pieces of dimensions of roughly 1 cm x 4 cm. The obtained pieces were cleaned by immersion in freshly prepared piranha solution (concentrated sulfuric acid / 30 w% aqueous hydrogen peroxide, 2/1 (V/V)) for 10 minutes followed by rinsing with deionized water and ethanol and drying in nitrogen stream. (**Handle with care!** Piranha solution is an extremely oxidizing agent; contact with any organic material, even residual solvent in a frit, must be avoided.) This cleaning step was conducted for all substrates employed, i.e. as blank or SAM-covered sample. Application of sonication for cleaning is not recommended as detachment of gold from silicon was observed.

Synthesis of PPN-6 films on electrodes

Following established procedures,[S1] as-cleaned gold substrates were then immersed in 20 ml of an ethanolic solution of 4-bromothiophenol (1 mmol/l), covered with argon in a screw cap glass bottle, sealed and placed in the dark for 16 hours. Thorough rinsing with ethanol and drying in nitrogen stream followed.

As-prepared SAM-covered gold substrates were employed for film polymerization within hours. A tubular reaction vessel with additionally added necks was dried by heating and outgassing , brought into a glove box and charged with bis(1,5-cyclooctadiene)nickel(0) (4.63 eq., 2.045 mmol, 562.5 mg), 2,2'-bipyridyl (4.60 eq., 2.035 mmol, 317.8 mg), dry DMF (42.5 ml), dry THF (42.5 ml) and 1,5-cyclooctadiene (4.66 eq., 2.059 mmol, 0.256 ml). This reaction mixture – so far without monomer – was stirred at room temperature until all components were dissolved completely. The reaction vessel was removed from the glove box and equipped with SAM-covered and blank gold substrates that were hold by a metal clamp attached to a wire that was pierced through a septum. The pieces were immersed into the reaction mixture from atop allowing the mixture to be stirred without any mechanical stress. At this point the monomer tetrakis(4-bromophenyl)methane (1.00 eq., 0.442 mmol, 281.2 mg) was added under argon flow. The PPN-6 protocol applied here allows the reaction mixture to be stirred at room temperature.[S2] Completion of the reaction was accompanied by a color change from deep violet to brown. Under argon atmosphere the reaction proceeded for 20 hours whereupon a formation of precipitate could clearly be observed. Reaction was quenched by slow addition of aqueous hydrochloric acid (6 mol/l, 30 ml) and stirring at room temperature until the color changed from brown over reddish to light bluish green which takes approximately 1.5 hours. Silicon wafer pieces were kept immersed during this time. Bulk precipitate was filtered off and washed with methanol, water (4 times, 20 ml each) and THF (two times, 20 ml) before being Soxhlet extracted from THF and dried in vacuum (110 °C, 16 hours). Repeated experiments always gave high yields of bulk precipitate around 90 %. The employed gold covered silicon wafers were washed and Soxhlet extracted accordingly but dried in vacuum at a lower temperature (60°C).

To monitor the adsorption of 4-bromothiophenol self-assembled monolayer (SAM) on a gold surface, Surface Enhanced Infrared Absorption Spectroscopic (SEIRAS) measurements were carried out in a Kretschmann-like Attenuated Total Reflection (ATR) configuration. Details about the ATR-FTIR set-up are given elsewhere.[S3] The removable single crystal silicon prism of the ATR cell was coated with a thin nanostructured gold film to obtain an adequate surface enhancement. FTIR spectra were recorded with a spectral resolution of 4 cm^{-1} on a Bruker IFS66v/s IR spectrometer equipped with a liquid nitrogen cooled photoconductive MCT detector. For each spectrum 400 scans were co-added.

For SAM-functionalization, the gold layer was incubated overnight with 2 ml of a 1 mmol/l ethanolic solution of 4-bromothiophenol inside the probe cell under argon atmosphere at room temperature. The polymerization reaction was then carried out by charging the probe cell with reaction mixture consisting of the amounts described above for the batch reaction divided by a factor of 42.4 which yielded a total volume of reaction mixture that complied with the confined space of the probe cell. This reaction mixture was prepared beforehand to ensure entire dissolution of all components before being applied to the probe cell. In contrast to the batch reaction, here the monomer was dissolved in THF before being added to the reaction mixture in the probe cell.

Geometry optimizations and frequency calculations for DFT were performed in vacuo on the BP86 / 6-31g* level of theory[S4] using Gaussian 09.[S5]

Synthesis of tetrakis(4-bromophenyl)methane:[S6]

A 50 ml round bottom flask was charged with bromine (20 eq., 125.8 mmol, 6.55 ml). At room temperature tetraphenylmethane (1 eq., 6.3 mmol, 2.10 g) was added as solid in small portions. The mixture was stirred at room temperature for 30 min and then cooled to -78 °C to add ethanol dropwise. After addition was completed, the mixture was allowed to reach room temperature overnight in the open flask. Solid was filtered off (frit, pore 5, vacuum) and washed with aqueous sodium thiosulfate solution (0.5 mol/l, 200 ml) and water (400 ml) to yield a brown-yellowish solid that was thoroughly dried in the frit. Residual water was removed *via* dissolution of the solid in THF and subsequent addition of sodium sulfate. The crude product was purified by column chromatography (n-pentane/dichloromethane: 93/7 (V/V)) to yield the product as white solid (3.45 g, 86 %).
NMR: ^{13}C ($CDCl_3$, 50 MHz) δ / ppm: 144.6, 132.5, 131.2, 121.0, 63.9. ^{1}H (CDCl3, 200 MHz) δ / ppm: 7.39 (dt, 8 H), 7.01 (dt, 8H).

Fig. S1 Photographs of as-purchased gold coated silicon wafer (a), of a blank sample (b) and SAM-functionalized sample (c) which were both subjected to the PPN-6 polymerization reaction.

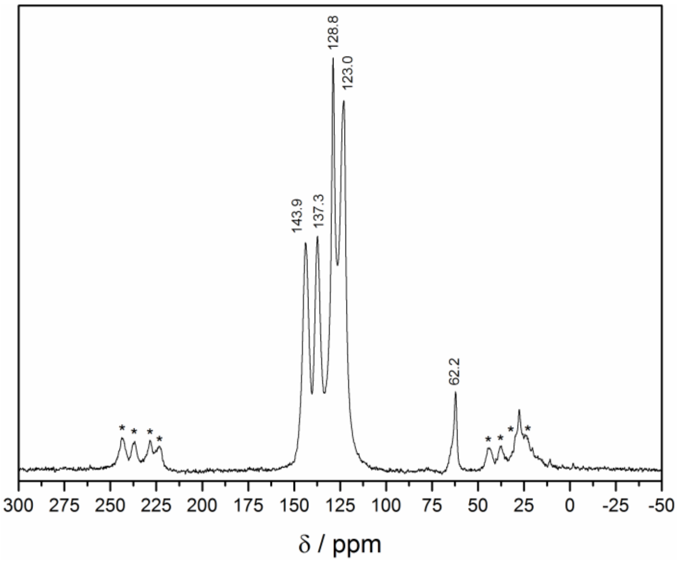

Fig. S2 Solid-state-MAS (10 kHz) NMR spectrum of PPN-6. Rotational sidebands are marked with an asterisk. The signal at around 28 ppm can be ascribed to residual THF.

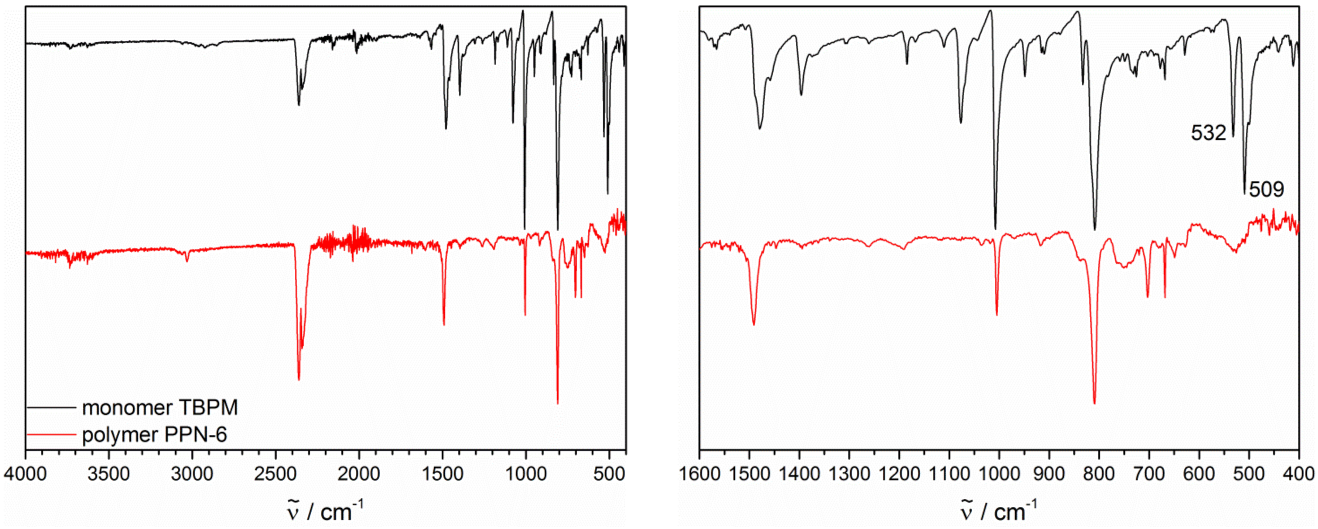

Fig. S3 ATR-FTIR spectra of monomer tetrakis(4-bromophenyl)methane (black line) and polymer PPN-6 (red line). Disappearance of the labeled signals is indicative of loss of bromine hence polymer formation.

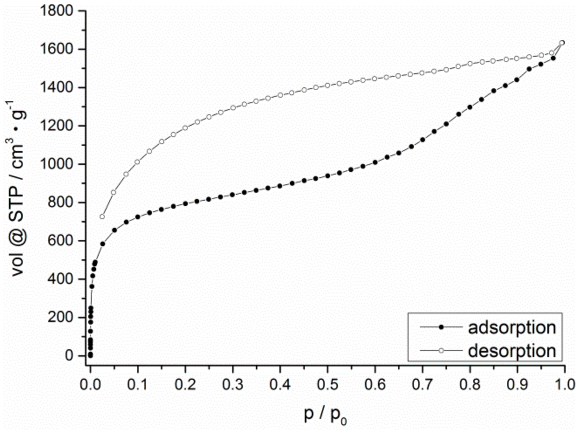

Fig. S4 Nitrogen sorption measurement on a bulk sample of PPN-6 that precipitated during the coating experiment. The obtained BET surface area is 2977 m^2/g.

Kr-Sorption measurements on PPN-6 films grown on SAM functionalized gold substrates

Krypton sorption measurements were repeatedly conducted on the PPN-6 films. However, due to the very low sample mass initially no data points could be obtained. Therefore, one measurement was carried out in which several films were combined (in total 16.9 cm^2 covered substrate) and subjected to the measurement chamber at once. As a result a 5-point krypton sorption measurement could be obtained (Figure S5). As the overall sample mass was still too low to be obtained by simple weighing, the measured surface area cannot be calculated as gravimetric surface area (a value usually given for bulk porous materials), but is related to the provided substrate surface. It should be further noted that the given film morphology (i.e. a thin, dense and homogeneous polymer layer plus a thicker polymer layer consisting of aggregated polymer particles) aggravate any meaningful estimation of the finally applied sample mass using film thickness, as the overall density of such films can just be assessed with high inaccuracy.

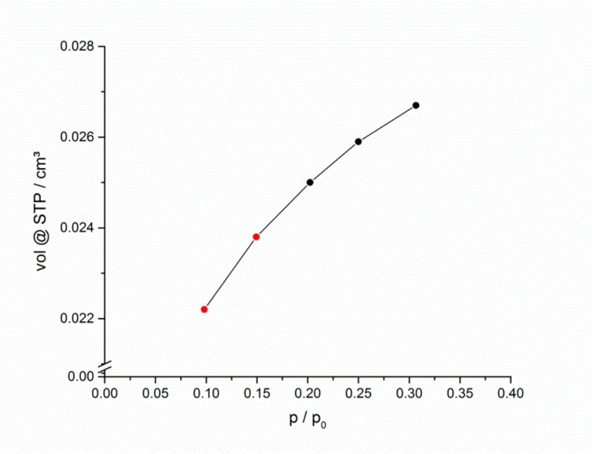

Fig. S5: Recorded data points for Kr-sorption measurement.

From the krypton sorption measurement a surface area of the films of 67.5 cm^2/cm^2 could be calculated. This shows that a porous polymer film was coated on the substrate. The BET plot for the points of the measurement meeting the criteria recommended by Rouquerol et al. (marked red in Figure S5) shows reasonable values for C and y-intercept.[S7]

Table S1: BET analysis data for the Krypton sorption measurement.

data points used	2	
C	278.189	
y-intercept	46.51	
slope	12892.972	
r	1.000000	
surface area	0.114	m²
provided sample area	16.9	cm²
surface area per sample area	67.5	cm²/cm²

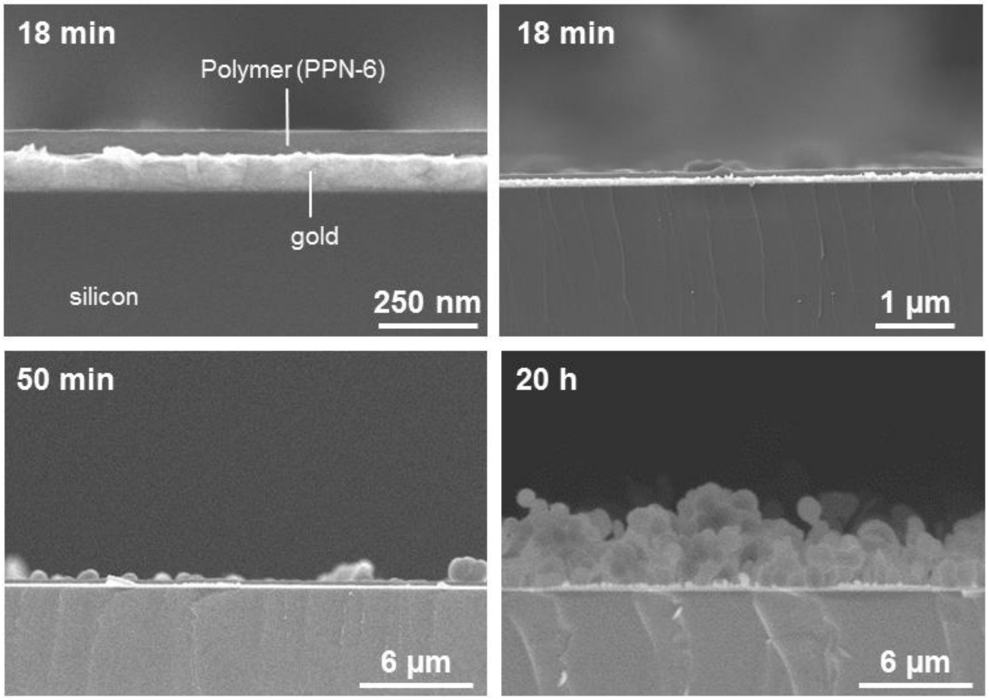

Fig. S6: SEM micrographs of PPN-6 film grown on gold substrate *via* Yamamoto cross coupling reaction after 18 min, 50 min and 20 h reaction time.

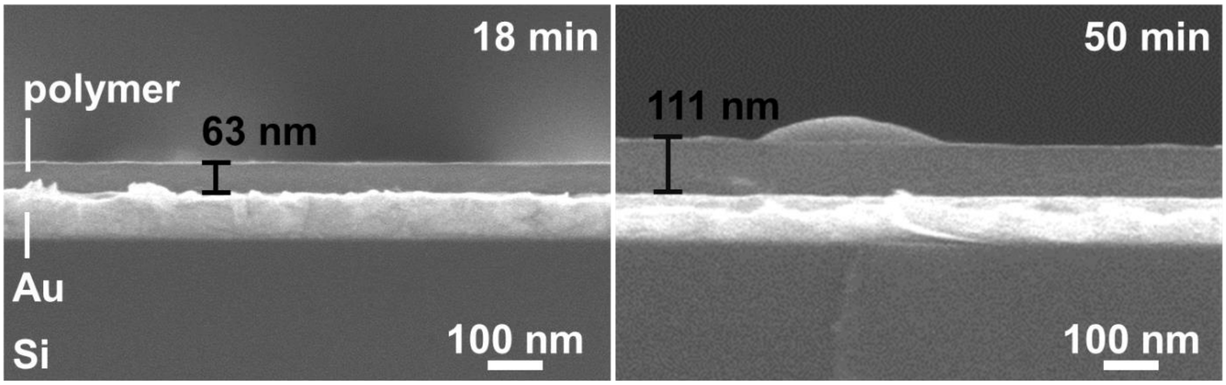

Fig. S7: SEM micrographs and measurement of the thickness of the primary polymer films of PPN-6 grown on gold substrates *via* Yamamoto cross coupling reaction after 18 and 50 min.

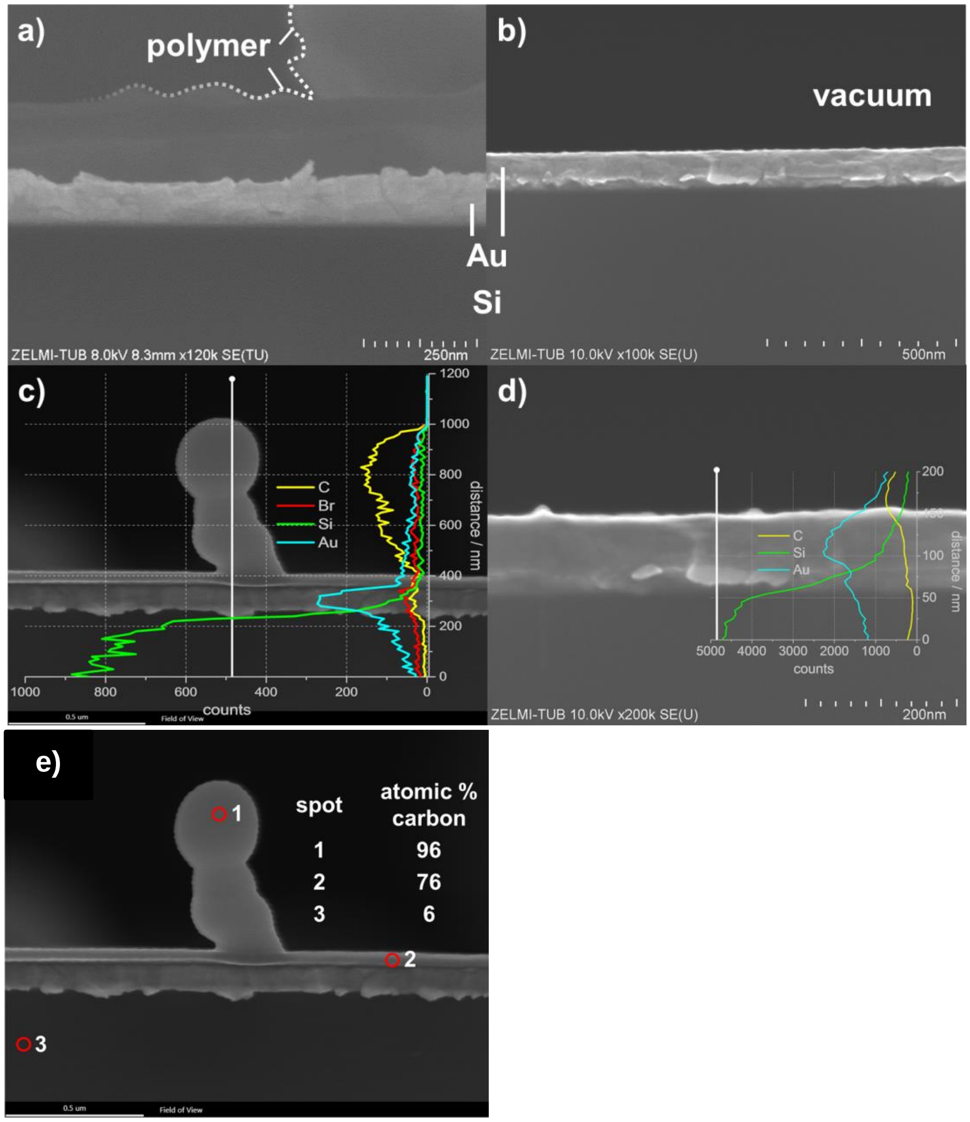

Fig. S8 SEM cross section micrographs with EDX line scan analyses of SAM-functionalized gold with polymer grown atop (a, c, e) and blank sample after polymer layer was detached by swelling and rinsing (b and d). Since no better contrast could be obtained in a), a white dotted line fading away to the left indicates the border between polymer and vacuum. The missing intensity of the carbon graph in c) in the region of the thin film is caused by the restricted resolution of EDX line scans. However, spot scan analysis e) clearly shows the carbonaceous nature also of the homogeneous film (spot 2).

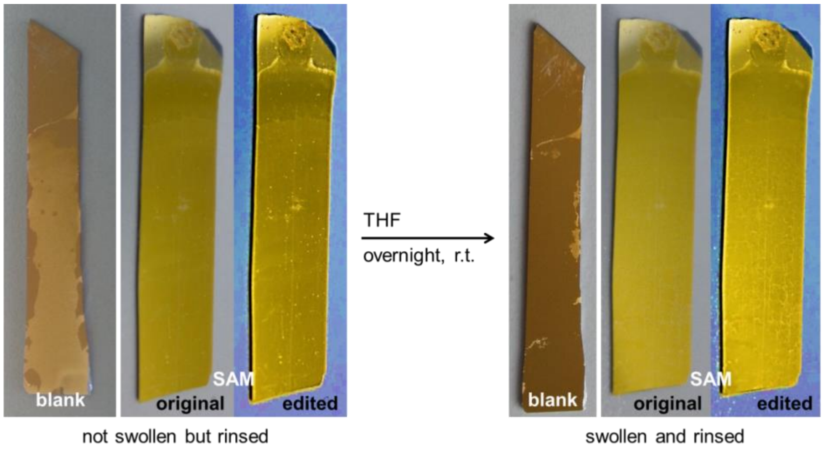

Fig. S9 A SAM-functionalized gold wafer with grown polymer film PPN-6 before (left) and after (right) swelling and rinsing with THF. For comparison one of the rare occasions were a polymer film was also deposited on a non-functionalized (blank) gold wafer is shown under the same treatment showing complete removal of the polymer film after THF washing. To increase the visibility of cracks after and also prove their absence before this procedure the SAM-pictures have been graphically edited.

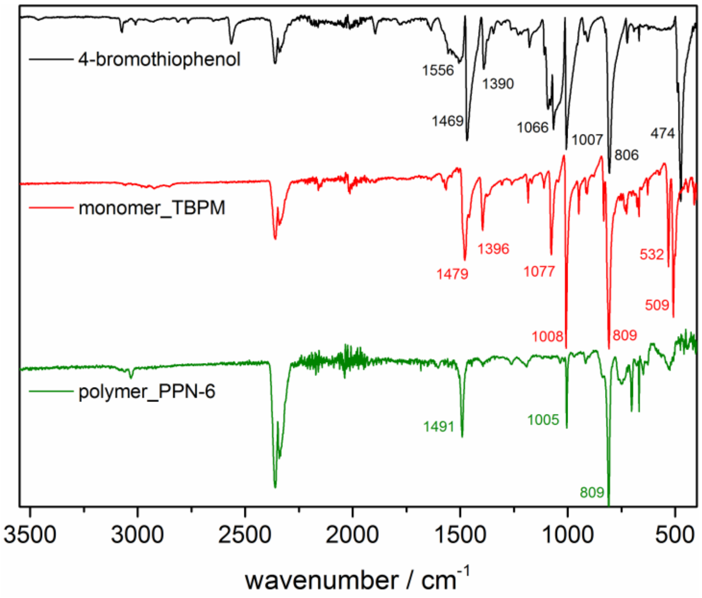

Fig. S10 FTIR-ATR spectrum of 4-bromothiophenol (black), TBPM (red) and PPN-6 (green).

DFT Calculations

Geometry optimizations and frequency calculations were performed in vacuo on the BP86 / 6-31g* level of theory[S4] using Gaussian 09.[S5]

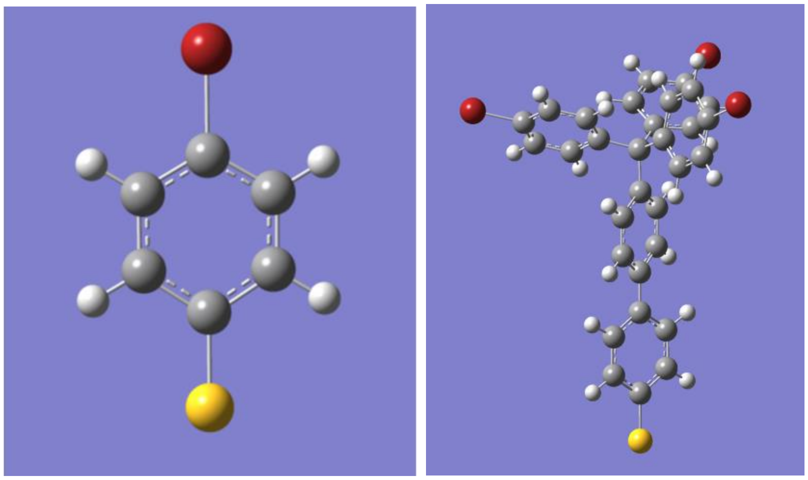

Fig. S11 Model structure of deprotonated 4-bromothiophenol (left) and of deprotonated SAM unit linked to one monomer species (right) for DFT calculations. Atom label: bromine (red), carbon (dark grey), hydrogen (light grey), sulfur (yellow)

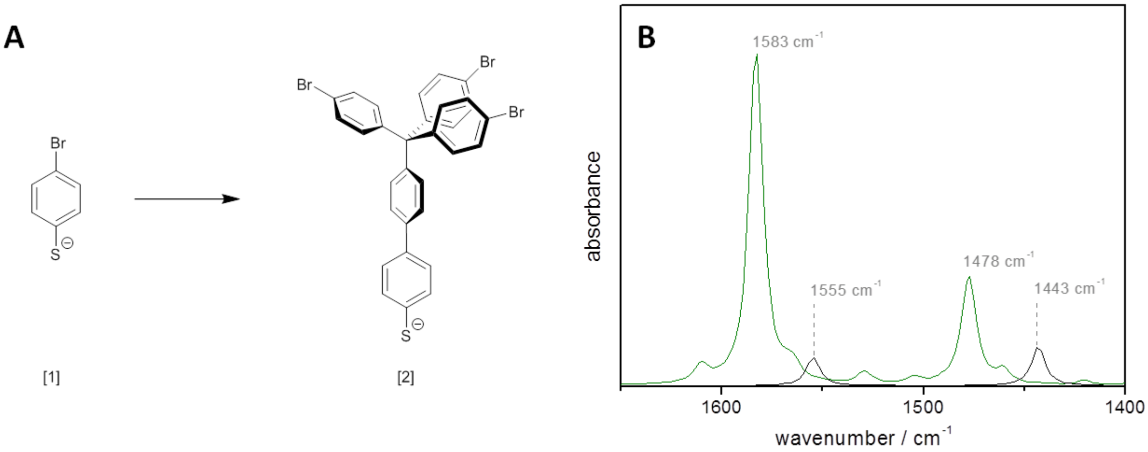

Fig. S12 Illustration of a deprotonated 4-bromothiophenol [1] and of one SAM-monomer unit after coupling [2] (A) and the corresponding DFT calculated spectra of [1] (black) and of [2] (green). The most intense bands are labeled.

References:

S1 (a) M. D. Porter, T. B. Bright, D. L. Allara and C. E. D. Chidsey, *J. Am. Chem. Soc.* **1987**, *109*, 3559; (b) C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides and R. G. Nuzzo, *J. Am. Chem. Soc.* **1989**, *111*, 321.

S2 W. Lu, D. Yuan, J. P. Sculley, D. Zhao, R. Krishna and H.-C. Zhou, *J. Am. Chem. Soc.* **2011**, *133*, 18126.

S3 (a) K. Ataka and J. Heberle, *J. Am. Chem. Soc.* **2003**, *125*, 4986; (b) N. Wisitruangsakul, O. Lenz, M. Ludwig, B. Friedrich, F. Lendzian, P. Hildebrandt and I. Zebger, *Angew. Chem. Int. Ed.* **2009**, *48*, 611.

S4 (a) J. P. Perdew, *Physical Review B* **1986**, *33*, 8822-8824; (b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; (c) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

S5 M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *Gaussian Inc., Wallingford, CT* **2009**.

S6 W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Blümel, R. Krishna, Z. Li and H.-C. Zhou, *Chem. Mater*. **2010**, *22*, 5964-5972.

S7 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603-619