

Electronic Supplementary Information for

A Heterotriangulene Polymer for Air-stable Organic Field-Effect Transistors

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1. Synthesis

4,4,8,8,12,12-hexamethyl-8,12-dihydro-4H-benzo[1,9]quinolizino[3,4,5,6,7-defg]acridine (DTPA) was synthesized according to literature from methyl 2-iodobenzoate and methyl 2-aminobenzoate. [1, 2]

2. Photoluminescence spectra of toluene vs. CHCl₃ solutions and the influence of UV-light exposure

Fig. S1 shows the photoluminescence spectra of 1g/L PTA in toluene and chloroform solution under different pre-conditions. The solid black line displays the fluorescence spectra of solutions which were prepared under ambient condition, under yellow light and kept in dark until the measurements (blue dashed line) and exposed to UV-light (~10 s, with wavelengths of 254 nm, 366 nm) (red dashed/dotted line). In contrast to the toluene solutions, the chloroform solutions spectra exhibit a significant influence of the ambient/UV-light exposure. A second peak appears around ~565 nm. The corresponding inset depicts a color change of the CHCl₃ solution from colorless to brown solution when exposed to ambient light. The observed effects can be ascribed to the dissociation of CHCl₃ under ambient light or UV-light at which hydrochloric acid (HCl) [5,6] is formed and protonation of the central nitrogen happens. Even if the CHCl₃ solution was prepared under yellow light and kept in dark, a non-negligible emission from 500 nm to 650 nm appears but is not as pronounced as for solutions prepared under ambient light or exposed to UV-light. This can be explained by short ambient light exposure during mounting the sample in the spectrofluorophotometer as well as the light influence during the measurements. Moreover, it cannot be excluded that the used CHCl₃ has already contained a small amount of HCl. The ~10 nm blue-shift of the emission maxima (at 434 nm) in comparison to the spectra of 0.005g/L solution shown in **Fig. 4** in the main text can be ascribed to the high concentration (1g/L) resulting in self absorption of these solutions.

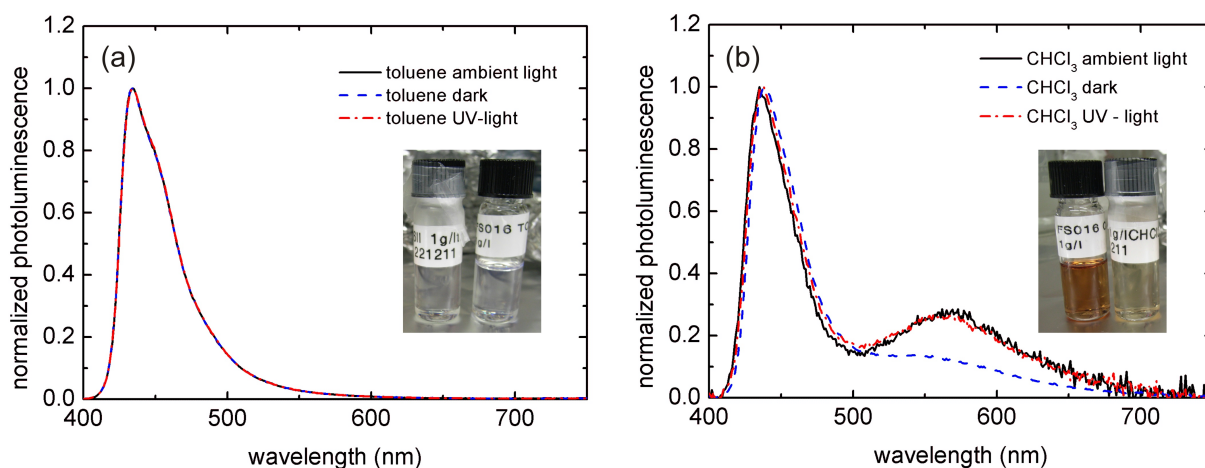


Fig. S1 Photoluminescence emission spectra of 1g/L PTA solution in toluene (a) and chloroform (b) after preparation under ambient conditions (black solid line), in dark (blue dashed line) and after exposure to UV-light (red dashed/dotted line). Inset: corresponding solutions when prepared under ambient light (left) and in dark (right).

3. Absorption and photoluminescence spectra of PTA films

Fig. S2 displays the UV/Vis absorption spectra and photoluminescence spectra of **PTA** films spin-coated from 2g/L toluene and chloroform solutions. The UV/Vis absorption maxima of **PTA** films were at 383 nm and 325 nm. The fluorescence spectrum of films prepared from toluene and CHCl_3 solution exhibits a maximum at 434 nm and 436 nm, respectively. Compared to the results obtained for **PTA** solutions, the spectra of films showed no significant influence of the used solvent, which can be explained by the fact that the solutions for film deposition were prepared and spin-coated under inert atmosphere in absence of UV-light (no discoloration, no protonation effects were observed). Subsequently the films were dried under high vacuum ($p \sim 4 \times 10^{-5}$ mbar) at 120°C to remove residual solvents.

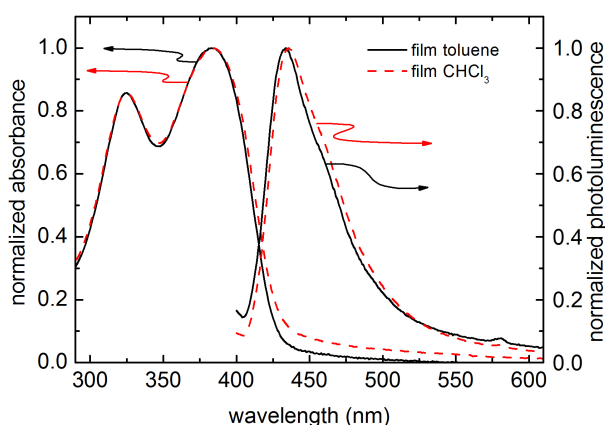


Fig. S2 UV/Vis absorbance and photoluminescence emission spectra of **PTA** films prepared from toluene (solid black line) and chloroform (dashed red line) solutions.

4. Surface morphology of a P3HT film

Fig. S3 shows the topographic image of a typical **P3HT** film on SiO_2 after annealing at 120°C for 1h in high vacuum ($p \sim 4 \cdot 10^{-5}$ mbar). The film exhibits a very smooth surface with a root-mean-squared roughness of ~ 0.4 nm.

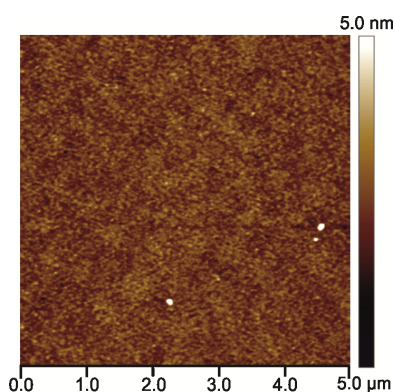


Fig. S3 AFM topographic image of a typical **P3HT** film on SiO_2 (scan size 5 μm x 5 μm).

5. Energy levels of P3HT and work function of differently treated Au

Fig. S4 shows the results of ultraviolet photoelectron spectroscopy (UPS) of the **P3HT** polymer to determine the absolute location of the energy levels of **P3HT** and the relative alignment at the interface to gold. The secondary electron cut-off was found at 4.2 eV with respect to the Fermi level (E_F) and, in conjunction with the binding

energy of the emission onset of 0.3 eV below the Fermi level, the corresponding ionization energy could be determined to 4.5 eV (see Fig. S4 (a)). The lowest unoccupied molecular orbital can be estimated ($E_{LUMO} = 2.6$ eV) by using the optical gap energy of 1.9 eV, which was determined from UV/Vis absorption measurements in solid state (film of 2g/l toluene, not shown). The corresponding energy level scheme is shown in Fig. S4 (b).

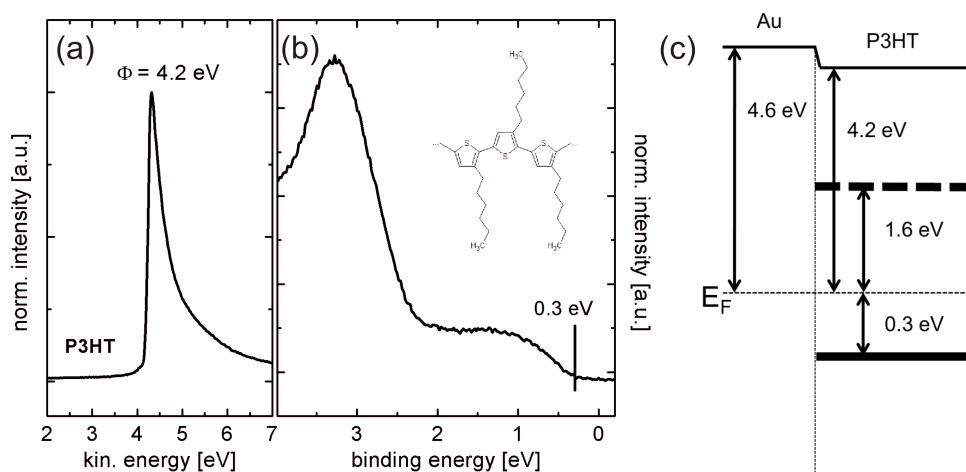


Fig. S4 (a) Secondary electron cut-off and (b) valence region UPS spectra of P3HT on Au/SiO₂ substrates. (c) Schematic energy levels of P3HT with respect to gold.

As mentioned in the main text, the work function of the gold with 4.6 eV is rather low. This can be explained by hydrocarbon contaminations on gold, which lower the surface dipole and therefore the work function. [3] Correspondingly, to determine the influence of different treatments and storing conditions on the work function of gold, various gold substrates were investigated. To resemble the conditions in the device after evaporation of gold, the sample was exposed to the lift-off chemicals used during the source/drain structuring process. The work function of these gold films subsequently stored in argon was determined to 4.58 eV (**Au**, **Table S1**). When the samples were stored in air (for ~2-3 days), the work function was lowered by about 0.15 eV (**Au_{air}**, **Table S1**). Films exposed to the lift-off chemicals, which were additionally treated with 15 min HMDS, revealed a work function of 4.53 eV (**Au^{HMDS}**). The highest work function of 4.65 eV (still low due to storing in air) was obtained for gold films without any additional treatment (**Au_{air}^{pristine}**, **Table S1**). The obtained values are in good agreement with results from literature. [3, 4]

Table S1: Work functions of differently treated gold films; **Au**: exposed to lift-off chemicals and stored in Ar, **Au_{air}**: exposed to lift-off chemicals and stored in air, **Au^{HMDS}**: exposed to lift-off chemicals and HMDS, then stored in Ar; **Au_{air}^{pristine}**: without treatment but stored in air.

Sample	Au	Au _{air}	Au ^{HMDS}	Au _{air} ^{pristine}
ϕ (eV)	4.58	4.43	4.53	4.65

6. Output characteristics of PTA based OFETs with different interface treatments

Fig. S5 depicts output characteristics of PTA based OFETs with UV/ozone (b) and O₂ plasma (c) treatment of the dielectric surface and the electrodes compared to a reference device without surface modification (a) (all samples were prepared without HMDS treatment). **Fig. S5 (b)** reveals that the UV/ozone treatment of the source/drain electrodes improves the charge carrier injection slightly seen by an improved linear characteristics at low drain voltages. Moreover, the channel current is lower which can be explained by a higher density of OH-groups on SiO₂ (caused by the UV/ozone exposure), leading to charge carrier trapping. The output

characteristics of OFETs with O₂ plasma exposure of the electrode-/dielectric surface show good saturation without injection problems (see Fig. S5 (c)), being mostly ascribed to (contact-) doping.

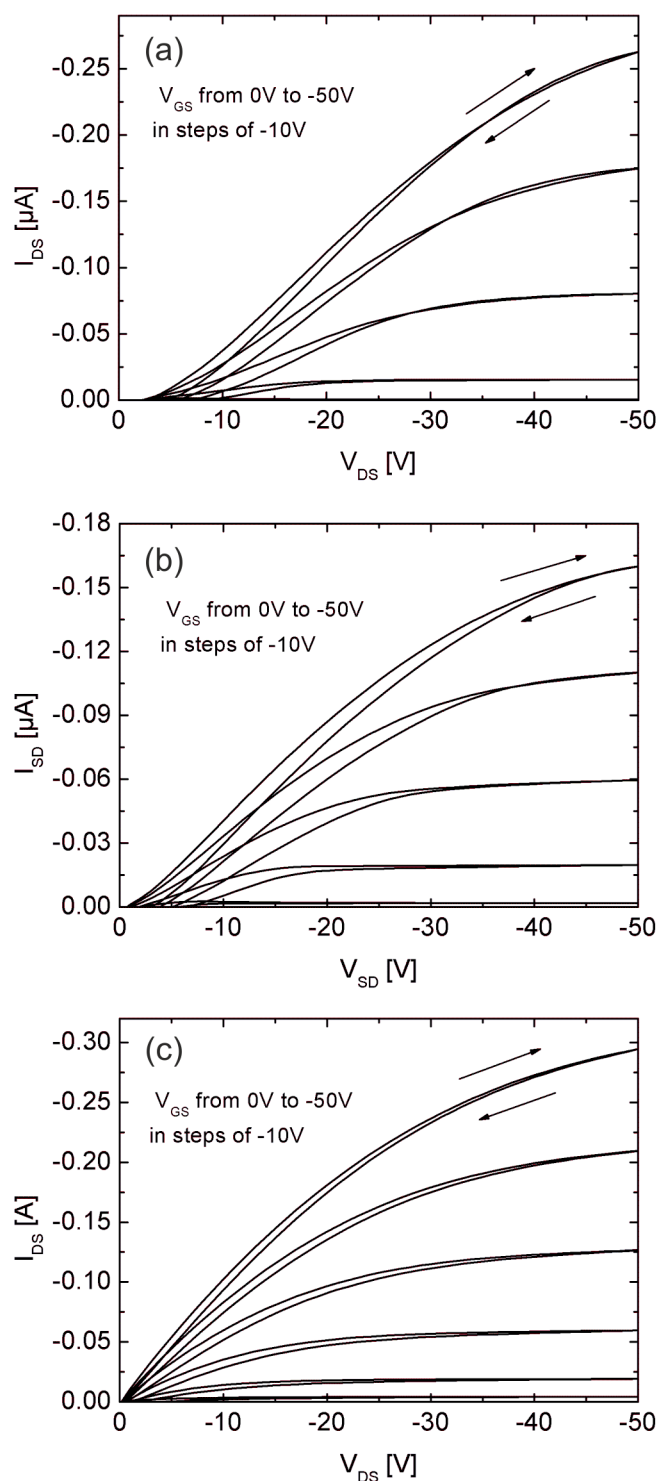


Fig. S5 Output characteristics of PTA OFETs with different interface treatments: (a) bare SiO₂, (b) UV/ozone and (c) O₂ plasma treatment, ($L = 25 \mu m$, $W = 2.85 mm$, without HMDS exposure).

7. Evolution of device parameters of PTA and P3HT OFETs under ambient conditions

Table S2 depicts the extracted device parameters of PTA and P3HT FETs over time when fabrication and characterization was done in air under ambient conditions. OFETs based on the novel polymer PTA did not show any significant change in performance even after storage over 3 months. Slight variations in field-effect mobilities and on/off ratios can be explained by varying levels of moisture and temperature. No degradation was observed, in contrast to P3HT devices, which exhibited gradually decreasing on/off ratios and increasing switch-on voltages due to doping effects.

Table S2: Device parameters of BG/BC OFETs based on PTA in comparison to P3HT after storage in air (23-26°C, 45-60 % rh).

Sample	time	Mobility μ_{sat}^a ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	I (on/off) ^b	V _{so} (V)
PTA	as prepared	6.6×10^{-4}	1.1×10^4	-4
	1 week	8.3×10^{-4}	2.5×10^4	-3
	1 month	7.6×10^{-4}	1.8×10^4	-3
	2 months	6.3×10^{-4}	1.1×10^4	-2
	3 months	6.3×10^{-4}	2.6×10^4	-1
P3HT	as prepared	2.5×10^{-4}	2.6×10^3	6
	1 week	2.7×10^{-4}	1.6×10^3	>10
	1 month	2.6×10^{-4}	3.2×10^2	>10
	2 months	2.1×10^{-4}	8.0×10^1	>10
	3 months	1.9×10^{-4}	6.6×10^1	>10

^a μ_{sat} was calculated according to the gradual channel approximation

^b on-current I_{on} was taken at $V_{\text{GS}}=-50\text{V}$, $V_{\text{DS}}=-50\text{V}$ and off-current I_{off} at $V_{\text{GS}}=0\text{V}$, and $V_{\text{GS}}=-10\text{V}$ (for P3HT OFETs, being fully depleted for as prepared devices), $V_{\text{DS}}=-50\text{V}$

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