Continuity of thin layers of organic semiconductor induced by modification of gate insulator

Adam Łuczak,*^a Witold Waliszewski,^a Krzysztof Jerczyński,^b Aleksandra Wypych-Puszkarz,^a, Jacek Rogowski,^c Joanna Pietrasik,^b Marcin Kozanecki,^a Jacek Ulański,*^a and Krzysztof Matyjaszewski,*^{a,d}

^a Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland

^b Institute of Polymer and Dye Technology, Faculty of Chemistry, Lodz University of Technology, Stefanowskiego 12/16, 90-924 Lodz, Poland

^c Institute of General and Ecological Chemistry, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland

^d Department of Chemistry, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213, USA.

Supporting information

OFET parameters calculation method

Parameter determination was a two-step process. In the first, the derivative of the $(I_{DS})^{1/2}$ curve (Ug) was calculated. Then the range in which this derivative took a constant value (with a small margin of error) was determined. This derivative formed the basis for calculating the mobility of charge carriers. In the second stage, a straight line with a slope consistent with the first derivative was determined, and the threshold voltage was calculated in this way (Fig. S1).

This way of determining the parameters allows to avoid the situation in which the model used is not satisfied, and then the calculated parameters are non-physical.



Figure S1. OFET transfer characteristics with a straight line intersecting the U_{gs} axis at U_{th} at the α angle fitted to the linear region of the curve (saturation regime of the OFET) and 1st derivative of this curve with marked range of the constant value corresponding to saturation regime of the OFET.

Charge carrier mobility in saturation was derived using the formula:

$$\mu_{sat} = \frac{2L}{WC_p} \left(\frac{d\sqrt{|I_{ds}|}}{dU_{gs}} \right)^2$$
(S1)

where W is the channel width, L is the channel length, C_p is the capacitance per area unit of the gate dielectric (5.3 × 10⁻⁵ F m⁻²), I_{ds} is drain current and U_{gs} is gate voltage. The charge carrier mobilities presented here are the average values obtained for 10 - 20 devices. The threshold voltage was estimated as the cross point of the fitted line and U_{qs} axis.

The ON/OFF ratio was calculated by dividing the I_{ds} current for the highest U_{ds} and U_{gs} voltages by the I_{ds} current for at the same U_{ds} and $U_{gs} = 0$ V

The subthreshold swing (SS) of the measured OFETs was determined as the reciprocal value of the slope of the fitting line to the subthreshold regime in the transfer curves of the OFETs.

$$SS = \frac{dU}{d(log(I_{DS}))} \text{ for } U_{GS} < U_{th}$$
(S2)

The density of trap states at the interface (N_{it}) was calculated using the equation:

$$N_{it} = \frac{C_p}{q^2} \left(\frac{q \, SS}{kT(ln10)} - 1 \right)$$
(S3)

In linear regime, charge carrier mobility was calculated using the formula:

$$\mu_{lin} = \frac{L}{WC_p U_{ds} dU_{gs}}$$
(S4)

For U_{ds} -5V and for maximum value of the U_{gs} .



Figure S2. AFM height images (10 μ m x 10 μ m) of neat PMMA dielectric layers (left) and PMMA layers with ca. 2.6 wt % of polymer star without the TiO₂ (right).

Table S1. Analysis of surface roughness of dielectric layers prepared from neat PMMA and from PMMA
containing various amount of TiO ₂ nanoparticles and ca. 2 wt% of polymer stars without the TiO ₂ .

TiO2@PSAN-b- PAA-PDVB concentration	Neat PMMA	0.2 wt%	0.4 wt%	0.6 wt%	0.8 wt%	1 wt%	Stars only ca. 2.6 wt%
Average value	2.3 nm	2.0 nm	2.5 nm	2.9 nm	2.8 nm	5.3 nm	1.4 nm
RMS roughness (S _q):	370 pm	473 pm	532 pm	818 pm	572 pm	972 pm	272 pm
Mean roughness (S _a):	294 pm	331 pm	379 pm	549 pm	370 pm	569 pm	217 pm
Maximum peak height (S _p):	1.9 nm	12.0 nm	8.0 nm	10.2 nm	7.5 nm	14.2 nm	3.1 nm
Maximum pit depth (S _v):	1.8 nm	1.8 nm	1.9 nm	2.7 nm	2.3 nm	4.2 nm	1.4 nm

Table S2. Linear regime charge carrier mobility calculated for the OFETs with semiconductor layer of 20 nm thick and with gate dielectric made of neat PMMA or of PMMA containing various amount of TiO_2 nanoparticles.

TiO₂@PSAN- b-PAA-PDVB concentration	ΡΜΜΑ	0.4 wt%	0.6 wt%	0.8 wt%	1 wt%
Charge carrier mobility [cm ² V ⁻¹ s ⁻¹]	0.08	3.52	1.25	0.91	0.95

Table S3. Subthreshold swing (SS) and charge trap density N_{it} calculated for the OFETs with semiconductor layer of 20 nm thick and with PMMA dielectric with different content of TiO₂ nanoparticles.

TiO₂@PSAN- <i>b</i> -PAA-PDVB concentration	ΡΜΜΑ	0.4 wt%	0.6 wt%	0.8 wt%	1 wt%
SS [V/dec]	6.26	1.90	2.35	5.04	5.06
N _{it} [eV ⁻¹ cm ⁻¹]	3.54x10 ¹²	1.05 x10 ¹²	1.31 x10 ¹²	2.85 x10 ¹²	2.85 x10 ¹²

Table S4. Linear regime charge carrier mobility calculated for the OFETs with various thickness of semiconductor layer and with gate dielectric made of PMMA containing 0.2 or 0.4 wt% of TiO_2 nanoparticles

TiO₂@PSAN-b- PAA-PDVB concentration	0.2 wt%			0.4 wt%			
Thickness of semiconductor [nm]	20	30	40	10	20	30	40
Charge carrier mobility [cm ² V ⁻¹ s ⁻¹]	0.065	2.52	2.01	0.0045	1.73	0.52	0.48

Table S5. Subthreshold swing (SS) and charge trap density N_{it} calculated for the OFETs with various thickness of the semiconductor layer and with PMMA dielectric containing 0.2 and 0.4 wt% of TiO₂ nanoparticles.

TiO ₂ @PSAN-b- PAA-PDVB concentration	0.2 wt%			0.4 wt%			
Thickness of semiconductor [nm]	20	30	40	10	20	30	40
SS [V/dec]	2.41	1.40	1.51	3.37	1.68	1.41	1.48
N _{it} [eV ⁻¹ cm ⁻¹]	1.34x10 ¹²	7.58x10 ¹¹	8.27x10 ¹¹	1.89x10 ¹²	9.25x10 ¹¹	7.71x10 ¹¹	8.12x10 ¹¹



Figure S3. Transfer and output characteristics of the OFETs prepared on Si/SiO₂ substrates; the C8-BTBT semiconductor layer was nominally ca. 50 nm thick.



Figure S4. Output characteristics of the OFETs with C8-BTBT semiconductor layer nominally ca. 20 nm thick and with dielectric layer made of neat PMMA or PMMA containing 0.4 % or 0.6% of TiO_2 . Straight lines are forward and dotted lines are backward sweeps; the last plot is a magnification of the curve measured for the sample with PMMA containing 0.6% TiO_2 .



Figure S5. Transfer characteristics of the OFETs with C8-BTBT semiconductor layer nominally ca. 20 nm thick, and with dielectric layer made of neat PMMA or PMMA containing 0.4 % or 0.6% of TiO_2 . Straight lines are forward and dotted lines are backward sweeps; the last plot is a magnification of the curve measured for the sample with PMMA containing 0.6% TiO_2 .



Figure S6. Transfer characteristic of the OFETs with C8-BTBT semiconductor layer nominally ca 20 nm thick, and with dielectric layer made of PMMA containing 0.6% TiO₂. The red line is the fitted line used to determine the threshold voltage; 1st derivative of the transfer curve. The fitted range in the transfer curve corresponds to the voltage range when the first derivative is constant.