

## Electronic Supplementary Information

### Redox active polymers with phenothiazine moieties for nanoscale patterning via conductive Scanning Force Microscopy

Ali Golriz<sup>a,b</sup>, Tassilo Kaule<sup>a</sup>, Jeannine Heller<sup>a</sup>, Maria B. Untch<sup>a</sup>, Philipp Schattling<sup>c</sup>, Patrick Theato<sup>c,d,e</sup>, Masaya Toda<sup>f</sup>, Shinya Yoshida<sup>f</sup>, Takahito Ono<sup>f</sup>, Hans-Jürgen Butt<sup>a</sup>, Jochen Stefan Gutmann<sup>b\*</sup>, Rüdiger Berger<sup>a\*</sup>

<sup>a</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany. E-mail: berger@mpip-mainz.mpg.de; Fax: +49-(0)6131-379-100; Tel: +49-(0)6131-379-114

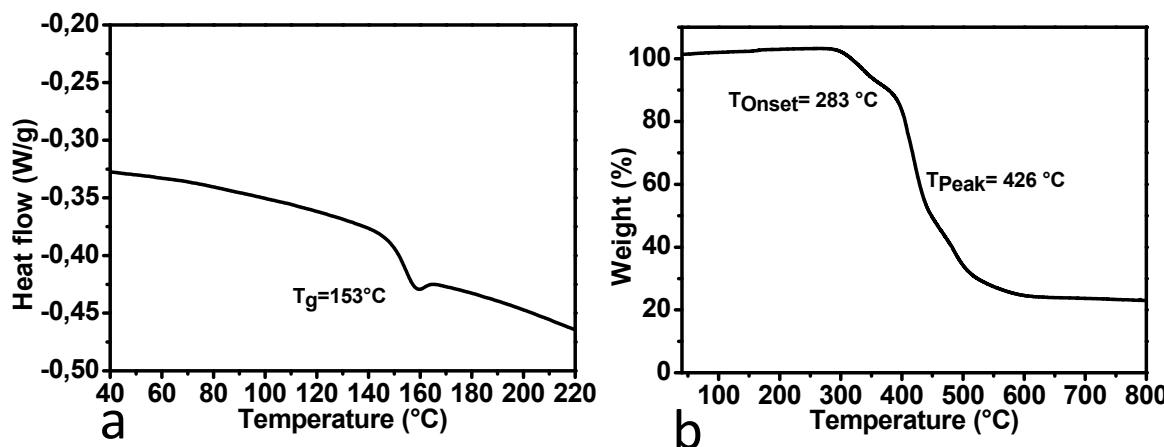
<sup>b</sup>Institute of Physical Chemistry, University of Duisburg-Essen, Universitätsstraße 2, D-45141 Essen, Germany. E-mail: jochen.gutmann@uni-due.de ; Fax: +49-(0) 201-183-4934; Tel: +49-(0) 201-183-2566

<sup>c</sup>Institute of Organic Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

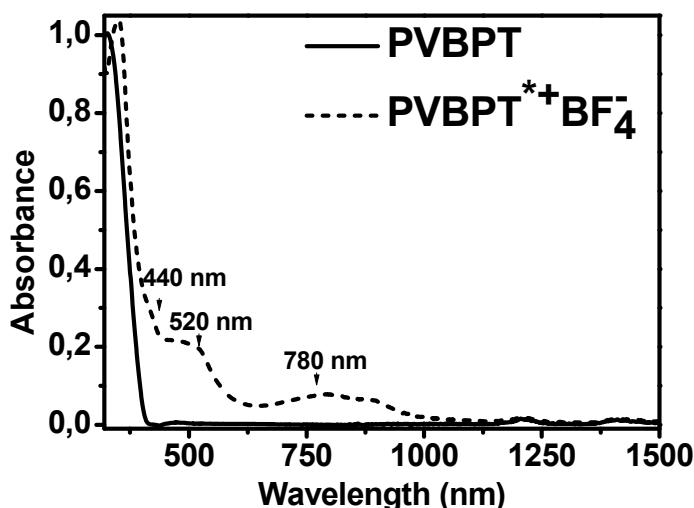
<sup>d</sup>Institute for Technical and Macromolecular Chemistry, University of Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

<sup>e</sup>WCU program of C2E2, School of Chemical and Biological Engineering, College of Engineering, Seoul National University, Seoul, Korea

<sup>f</sup>Graduate School of Engineering, Tohoku University, 6-6-01 Aza-Aoba, Aramaki, Aoba-Ku, Sendai, Miyagi 980-8579, Japan



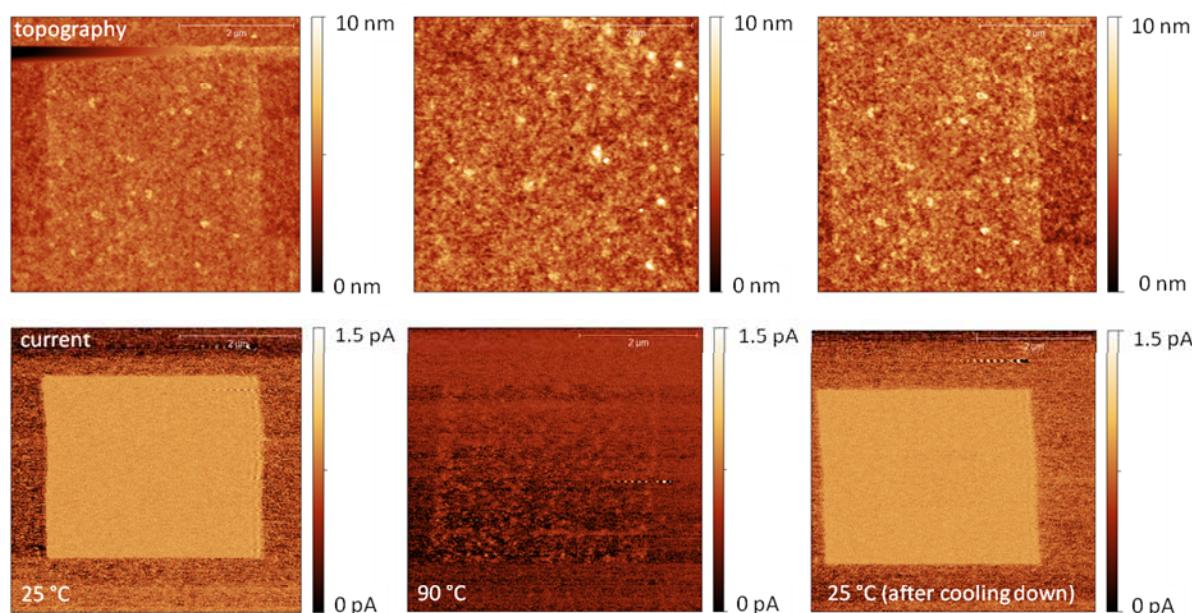
S1 a) Differential Scanning Calorimetry (DSC) Measurement at nitrogen atmosphere (30 ml/min) at a heating rate of 10 °C/min from 40 to 220 °C for PVBPT with MW ≈ 13.400 g/mol and PDI ≈ 1.43 . b) Thermogravimetry (TG) in nitrogen atmosphere (30 ml/min) at a heating rate of 10 °C/min from 40 to 800 °C for PVBPT with MW ≈ 13.400 g/mol and PDI ≈ 1.43.



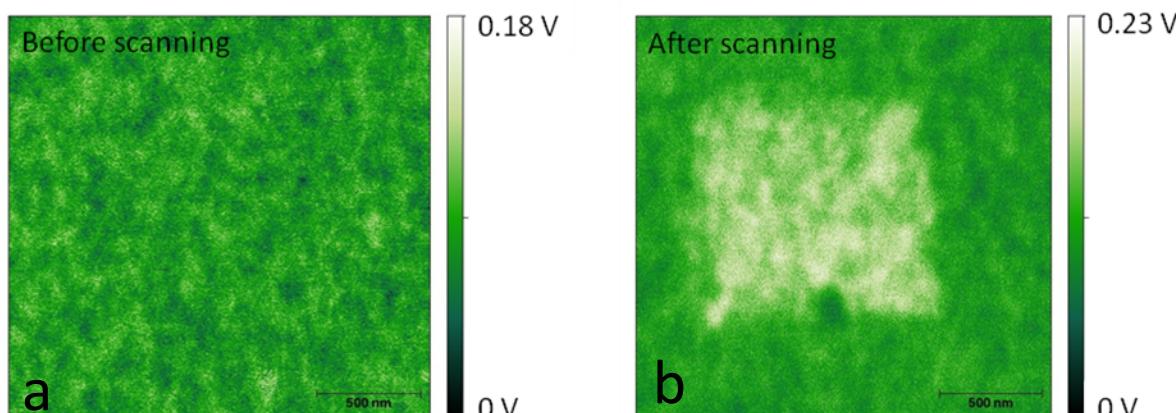
S2 By Addition of the oxidation agent  $\text{NOBF}_4$ , the oxidized polymer  $\text{PVBPT}^{*+}\text{BF}_4^-$  can be obtained as radical polymer cation with  $\text{BF}_4^-$  as counter ion. The deeply red colored polymer shows a characteristic absorption maximum at around 440 nm and 520 nm and smaller maximum at around 780 nm. These values correspond to the absorption bands observed for the phenothiazine radical cation.<sup>1,2</sup>

**S3** Current differences obtained for the region patterned with  $V_W = +10$  V at different reading bias potentials  $V_R$ . A pattern of  $1.2 \mu\text{m} \times 1.2 \mu\text{m}$  was written at the speed of  $0.3 \mu\text{m}/\text{s}$ . Then, after zoom out to  $3 \mu\text{m}^2$ , the surface was mapped while applying  $V_R$ . The current differences were obtained from the mean current profiles over the complete image, as shown in figure 3.

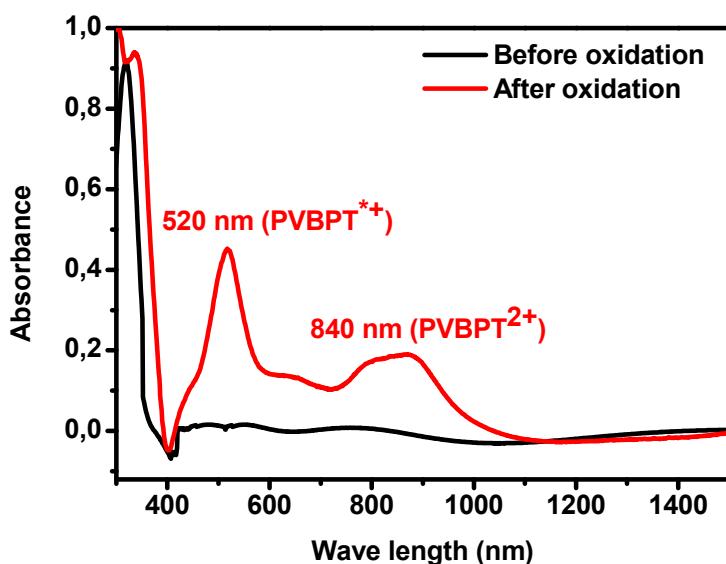
Reading bias (V)	Current difference (fA)
4	<b><math>0 \pm 95</math></b>
2	<b><math>0 \pm 95</math></b>
-1	<b><math>0 \pm 95</math></b>
-3	<b><math>20 \pm 95</math></b>
-4	<b><math>90 \pm 90</math></b>
-5	<b><math>280 \pm 82</math></b>
-6	<b><math>530 \pm 23</math></b>



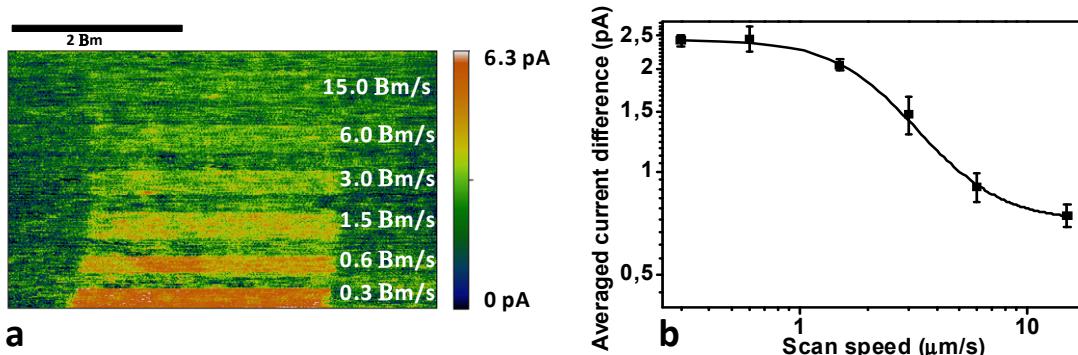
**S4** To prove the role of the water meniscus, we carried out patterning experiments at different temperatures. Three patterns were written and read out at  $25^\circ$  and  $90^\circ$  and after cooling to  $25^\circ$  using a heatable stage in a glove back (streamed with N2, humidity at approximately 2 %) respectively. We could observe a pattern at ambient temperature (an increase of  $510 \pm 65$  fA) whereas under the same patterning conditions the pattern written at  $90^\circ\text{C}$  was not visible (an increase of below  $50 \pm 81$  fA). After cooling down the sample, we could repeat the patterning successfully under controlled ambient conditions again (an increase of  $520 \pm 77$  fA). No significant change in topography was observed for all patterning experiments. The images show the topography and current map of spin coated PVBPT ( $45 \pm 7$  nm) on gold scanned with  $+10$  V on  $3.7 \mu\text{m} \times 3.2 \mu\text{m}$  at the speed of  $0.3 \mu\text{m}/\text{s}$ . The written pattern was read out with  $-6$  V at a speed of  $5 \mu\text{m}/\text{s}$  after zoom out.



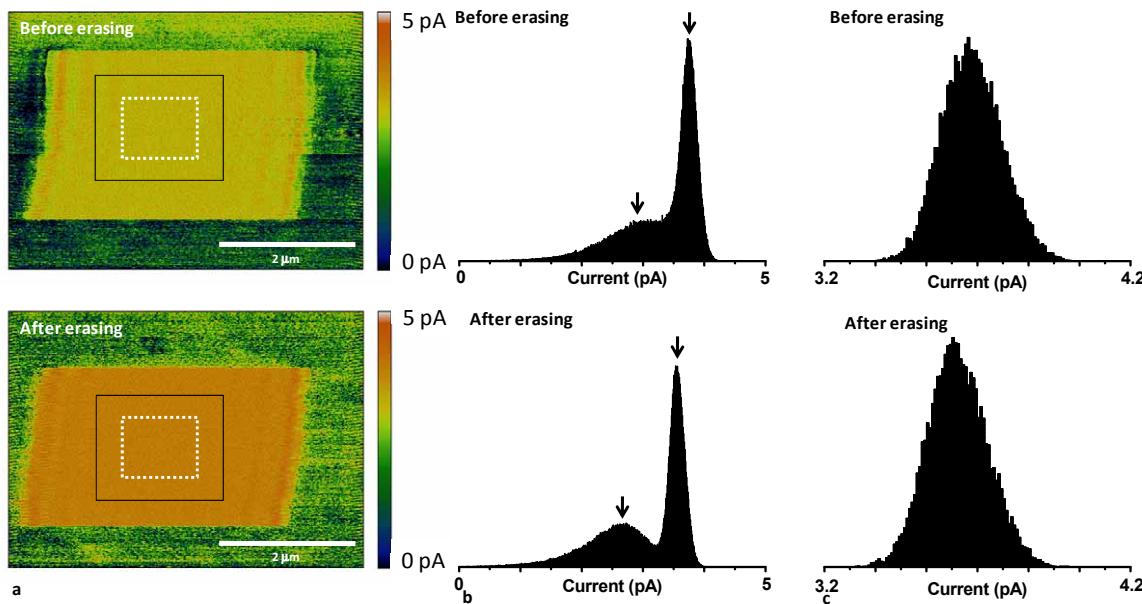
**S5** To prove the formation of the oxidized species, we performed . If the oxidation takes place, a net positive charge should be formed on the surface of the PVBPT film because of the formation of the cation species. KPFM was done following the frequency modulation method described by Zerweck et al.<sup>3</sup> The frequency was modulated at 3 kHz with driving amplitude of 3 V. KPFM measurements were done before (a) and after (b) writing on a scan area of 2  $\mu\text{m} \times 2 \mu\text{m}$  with a scan speed of 2  $\mu\text{m}/\text{s}$ . In order to prevent drift effects, we did the writing in tapping mode at +3 V sample bias on a scan area of 1  $\mu\text{m} \times 1 \mu\text{m}$ . The tapping set point was set to 0.1 V in order to have a quasi contact. For KPFM we used PPP-EFM cantilevers (Nanosensors, Neuchatel, Switzerland, nominal resonance frequency 75 kHz, conductive Pt/Ir coating). Before writing we see an all-over potential with an average value of 103 mV over the whole surface (Fig S5 a) After writing we observed a square in the KPFM image with potential increase of 54 mV compared to the nonwritten area (Fig S5 b). This indicates a positive net charge at the surface.



**S6** UV-Vis measurements of a spin coated PVBPT film (45 nm) on 100 nm ITO before and after the electrochemical oxidation via Cyclic Voltammetry. A bias of +1.5 V was applied to the spin coated film as the working electrode in a 0.1 M tetrabutylammonium tetrafluoroborate in dry acetonitrile. A Pt wire and a Ag/AgCl electrode were used as the counter and reference electrode, respectively. The characteristic bands at 520 nm and 840 nm correspond to the formation of the radical cation and dication, respectively<sup>4</sup>.



**S7** a) Current map of spin coated PVBPT (Thickness:  $30 \pm 5 \text{ nm}$ ) on gold patterned with  $+10 \text{ V}$  at different scanning speed on  $3 \mu\text{m} \times 0.3 \mu\text{m}$ . The patterns have an additional spacing of  $160 \text{ nm}$ . The read out was done by applying  $-6 \text{ V}$  after zoom out at the speed of  $5 \mu\text{m/s}$ . b) Logarithmic plot showing the dependency of current difference for the patterned and non patterned areas by variation of the scanning speed. The difference in conductivity changes within approximately  $130 \pm 12 \text{ nm}$  from  $2.42 \pm 0.44 \text{ pA}$  to  $4.97 \pm 0.31 \text{ pA}$  for the area that has been patterned with  $0.3 \mu\text{m/s}$ . In addition the spacing of  $160 \text{ nm}$  between the scans demonstrates clear distinction of the patterned and the non patterned area. Furthermore the current difference between the patterned and the non patterned areas increases, when the writing velocity is decreased from  $15 \mu\text{m/s}$  to  $0.3 \mu\text{m/s}$ . The averaged current difference increases and reaches its saturation point as expected with decreasing scanning speed. At this point the current difference does not significantly change when the writing speed is reduced from  $0.6$  to  $0.3 \mu\text{m/s}$  (from  $2.45 \pm 0.28 \text{ pA}$  to  $2.42 \pm 0.19 \text{ pA}$ ). Even between  $1.5$  and  $3.0 \mu\text{m/s}$  a current difference of around  $1.50 \pm 0.33$  to  $1.9 \pm 0.32 \text{ pA}$  can still be detected. Above  $6.0 \mu\text{m/s}$  the current difference decreases below  $0.91 \pm 0.17 \text{ pA}$ . Between  $6.0$  and  $15 \mu\text{m/s}$  the decrease in current difference is quite low ( $0.16 \pm 0.11 \text{ pA}$ : from  $0.91 \pm 0.17 \text{ pA}$  to  $0.74 \pm 0.28 \text{ pA}$ ). Therefore we could state that the slower the scanning speed the more of the PVBPT can be oxidized. Consequently electron transfer can take place more efficiently which then increases the conductivity of PVBPT. When all redox sites are oxidized the maximum of the conductivity is reached and no further increase can take place.



**S8** a) Current map of spin coated PVBPT on gold scanned with  $+10 \text{ V}$  on  $4.0 \mu\text{m} \times 2.2 \mu\text{m}$  at the speed of  $0.3 \mu\text{m/s}$ . The written pattern was read out with  $-6 \text{ V}$  at a speed of  $5 \mu\text{m/s}$  after zoom out. To erase the pattern partially a bias of  $-12 \text{ V}$  applied on a region of  $1.0 \mu\text{m} \times 0.9 \mu\text{m}$  at the speed of  $0.1 \mu\text{m/s}$  (whitely dashed line). b) Current histograms of the entire current map as shown in figure a. Left arrow shows the position of the current maximum in the non patterned region whereas the right arrow identifies the current maximum of the patterned region. c) Current histograms of the area in the region marked with a black line ( $2.0 \mu\text{m} \times 1.6 \mu\text{m}$ ) around the erased area. In the current map the written (oxidized) area can be clearly identified as a rectangular structure. Due to the low scanning speed a drift towards the left occurred during the scan. Before and after erasing the patterned area showed a current of  $820 \pm 131 \text{ fA}$  and  $840 \pm 108 \text{ fA}$  higher compared to the none patterned regions in the current map, respectively. Besides there is no significant in the Full Width at Half Maximum (FWHM) before and after erasing ( $280 \text{ fA}$  before and  $275 \text{ fA}$  after). This also indicates that no current change takes place due to the reduction process.

---

## References

- <sup>1</sup>P. C. Dwivedi, K. G. Rao, S. N. Bhat, C. R. Rao, *Spectrochimica Acta*, 1975, **31**, 129
- <sup>2</sup>D. Sun, S. V. Rosokha, J. K. Kochi, *J. Am. Chem Soc.*, 2004, **126**, 1388
- <sup>3</sup>U. Zerweck, C. Loppacher, T. Otto, S. Grafström, L. M. Eng, *Phys. Rev. B*, 2005, **71**, 125424
- <sup>4</sup>Y. Morishima, I. Akihara, S. I. Nozakura, *J. Polym. Sci.*, 1985, **23**, 661